# TOXIC SUBSTANCES FROM COAL COMBUSTION -- A COMPREHENSIVE ASSESSMENT

Quarterly Technical Report

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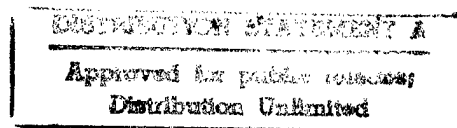
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# ABSTRACT

The Clean Air Act Amendments of 1990 identify a number of hazardous air pollutants (HAPs) as candidates for regulation. Should regulations be imposed on HAP emissions from coal-fired power plants, a sound understanding of the fundamental principles controlling the formation and partitioning of toxic species during coal combustion will be needed. With support from the Federal Ener gy Technology Center (FETC), the Electric Power Research Institute, and VTT (Finland), Physical Sciences Inc. (PSI) has teamed with researchers from USGS, MIT, the University of Arizona (UA), the University of Kentucky (UKy), the University of Connecticut, and Princeton University to develop a broadly applicable emissions model useful to regulators and utility planners. The new Toxics Partitioning Engineering Model (ToPEM) will be applicable to *all* combustion conditions including new fuels and coal blends, low-$NO_x$ combustion systems, and new power generation plants. Development of ToPEM will be based on PSI's existing Engineering Model for Ash Formation (EMAF). During the past quarter the final program coal, from the Wyodak seam in the Powder River Basin, was acquired and distributed. Extensive coal characterization and laboratory work is underway to develop and test new sub-models. Coal characterization in the past quarter included direct identification of the modes of occurrence of various trace inorganic species in coal and ash using unique analytical techniques such as XAFS analysis and selective leaching. Combustion testing of the bituminous coals continued and additional data were obtained on trace element vaporization in the combustion zone. Studies of post-combustion trace element transformations, such as mercury speciation in the flue gas, were also begun in the last quarter.

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# SECTION 1

# EXECUTIVE SUMMARY

# 1. EXECUTIVE SUMMARY

The technical objectives of this project are:

a.  To identify the effect of the mode-of-occurrence of toxic elements in coal on the partitioning of these elements among vapor, submicron fume, and fly ash during the combustion of pulverized coal,

b.  To identify the mechanisms governing the post-vaporization interaction of toxic elements and major minerals or unburnt char,

c.  To determine the effect of combustion environment (i.e., fuel rich or fuel lean) on the partitioning of trace elements between vapor, submicron fume, and fly ash during the combustion of pulverized coal,

d.  To model the partitioning of toxic elements between various chemical species in the vapor phase and between the vapor phase and complex aluminosilicate melts,

e.  To develop a frame work for incorporating the results of the program into the Engineering Model for Ash Formation (EMAF).

A description of the work plan for accomplishing these objectives is presented in Section 2.1 of this report.

The work discussed in this report highlights the accomplishments of the fifth quarter of this program. These accomplishments include the acquisition and distribution of the final Phase I program coal. In the ongoing coal characterization efforts XAFS and selective leaching were used to determine the forms of occurrence of various trace elements. Combustion experiments were performed at two different scales to explore vaporization of trace elements in the combustion zone. Combustion experiments were also begun on several scales to evaluate trace element transformations in the post-combustion zone.

Specifically, the final program coal, from the Wyodak seam of the Powder River Basin, was acquired from ABB. This coal is currently being used in a DoE funded program to evaluate ESP performance. The coal was then distributed to all team members and stored under argon.

XAFS analysis was utilized to measure the forms of occurrence of zinc and selenium in selected program coals. For example, this technique was used to show that selenium is primarily associated with pyrite in the Pittsburgh coal. In the Elkhorn/Hazard this element is primarily organically associated. Preliminary data were also obtained from the selective leaching procedure performed earlier in the program on the three bituminous coals. These data indicate that a significant portion of the arsenic in the Elkhorn/Hazard coal was not leached by any of the solvents used in the USGS leaching protocol. Comparison of the leaching and XAFS data suggest that the unleached portion may be due to extremely fine pyrite inclusions. In the other

bituminous coals the leaching data suggest that the arsenic was primarily associated with the pyrite -- corroborating the earlier XAFS findings for these coals.

Combustion experiments in the past quarter focussed primarily on vaporization of trace elements in the combustion zone. Size and density fractions of all three coals were burned in the MIT droptube furnace and size segregated ash samples were collected. Utility grind samples of the Pittsburgh, Elkhorn/Hazard, and Illinois No. 6 coals were burned under baseline (stoichiometric ratio of 1.2) conditions in the PSI entrained flow reactor (EFR). Data from the MIT experiments were compared with earlier data presented by Quann[1] and found to follow similar vaporization trends. The PSI data showed that the degree of vaporization was higher for the combustion experiments performed under fuel lean conditions.

Experiments were also begun to explore post-combustion trace element partitioning. These experiments included preliminary combustion experiments on the self-sustained combustor at UA, mercury speciation measurements at PSI, and the development of an experimental apparatus to measure mercury absorption on coal chars. The experiments on the laboratory-scale combustor were performed by a joint team of PSI and UA investigators and served to 'shake-down' the system and prepare the UA investigators for sampling with the Berner Low Pressure Impactor (BLPI). Preliminary mercury speciation measurements in flue gas from combustion of the Illinois No. 6 coal under baseline conditions at PSI were performed using the Ontario-Hydro method. This method was recommended by investigators in the ongoing program to evaluate methods for measuring mercury speciation in flue gas being performed by DoE, the Electric Power Research Institute (EPRI), and the University of North Dakota Energy and Environmental Research Center (UNDEERC). Preliminary data suggest that there is a much lower fraction of oxidized mercury present at temperatures below 750 K than predicted from equilibrium. To study mercury uptake by residual carbon in combustion systems, chars were produced from the three bituminous coals in the program and characterized by XAFS to determine the forms of sulfur present in the chars. The experimental apparatus to study mercury uptake on chars was designed and fabricated at UA during the last quarter.

# SECTION 2

## INTRODUCTION AND PROGRAM OVERVIEW

## 2. INTRODUCTION AND PROGRAM OVERVIEW

Before electric utilities can plan or implement emissions minimization strategies for hazardous pollutants, they must have an accurate and site-specific means of predicting emissions in all effluent streams for the broad range of fuels and operating conditions commonly utilized. Development of a broadly applicable emissions model useful to utility planners first requires a sound understanding of the fundamental principles controlling the formation and partitioning of toxic species during coal combustion (specifically in Phase I, As, Se, Cr, and possibly Hg). PSI and its team members will achieve this objective through the development of an "Engineering Model" that accurately predicts the formation and partitioning of toxic species as a result of coal combustion. The "Toxics Partitioning Engineering Model" (ToPEM) will be applicable to all conditions including new fuels or blends, low-$NO_x$ combustion systems, and new power systems being advanced by DOE in the Combustion 2000 program.

Based on a goal of developing and delivering this ToPEM model, a 5-year research program was proposed. This program is divided into a 2-year Phase I program and a 3-year Phase II program. The objective of the ongoing Phase I program is to develop an experimental and conceptual framework for the behavior of selected trace elements (arsenic, selenium, chromium, and mercury) in combustion systems. This Phase I objective will be achieved by a team of researchers from MIT, UA, UKy, Princeton University, the University of Connecticut, and PSI. Model development and commercialization will be carried out by PSI.

Our general approach to the development of the ToPEM model is to break the process for toxic formation into sub-processes, each of which will be addressed by team members who are experts in the area. Ultimately, this will result in new sub-models which will be added to the existing Engineering Model for Ash Formation (EMAF) to create ToPEM. Figure 2-1 illustrates the relationship between the elements of the Phase I work breakdown structure and the sub-processes. Each of the areas identified in the figure will be addressed in the Phase I program as described below.

Program Overview

*Forms of Occurrence of Trace Elements in Coal*

One of the most important questions to be answered in the program as a whole is whether the form of a particular element in the coal affects its form of emission at the end of the process. The answer to this question will determine the shape of the sub-models that must be developed in this program. Thus, a detailed understanding of the forms of individual trace elements in coal provides a foundation for much of the rest of the program. Key issues that are being addressed in Phase I are the specific mineral associations of individual elements and the relationship between trace metal form and "standard" analyses.

Because of the importance of elemental form (e.g., sulfate versus silicate mineral) on partitioning, it is critical that coals representing a broad range of elemental forms be examined in this program. In Task 2 we selected and acquired a total of four coals for study in this program.
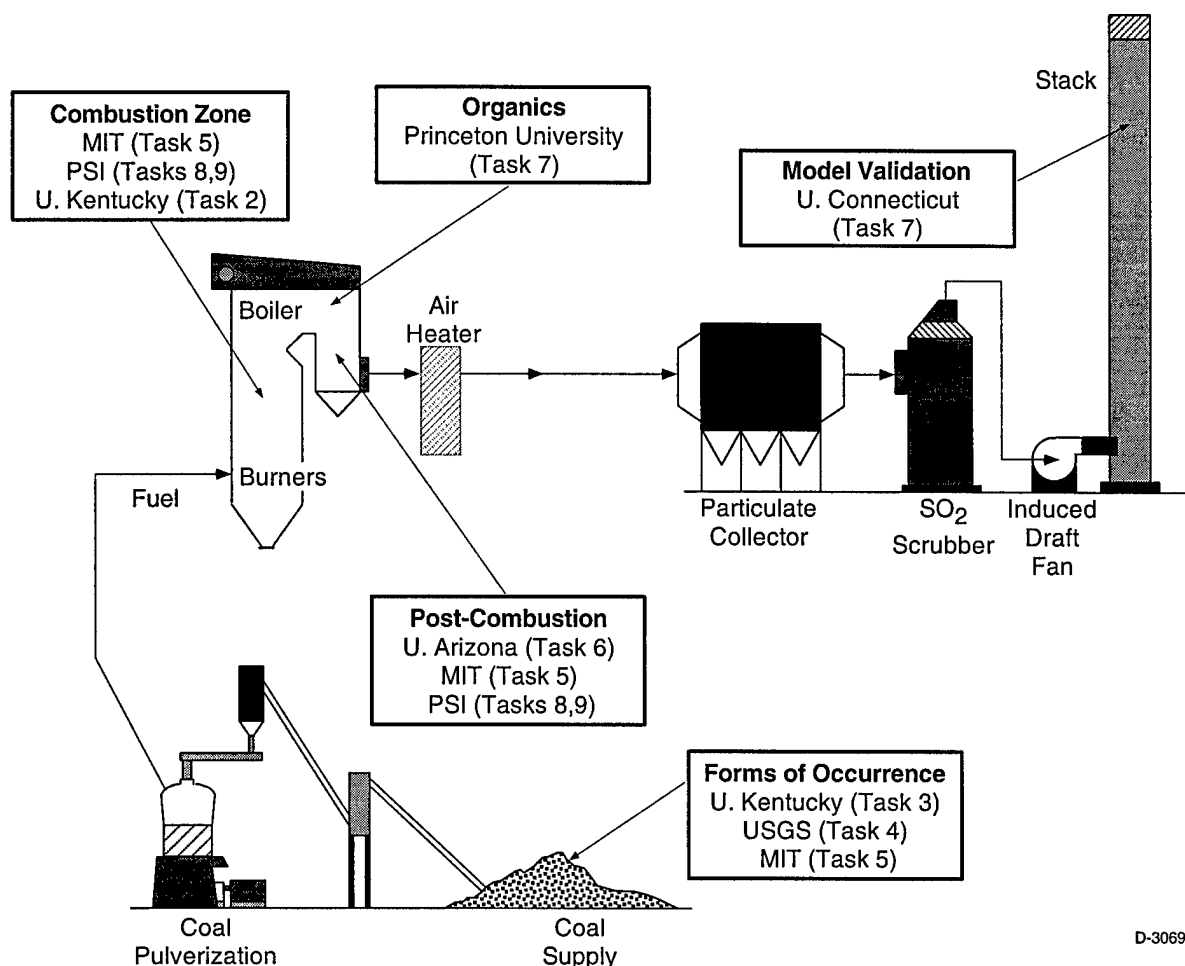
Figure 2-1. Project organization.

The coals chosen (1) represented a broad range of elemental forms of occurrence; (2) represented the major coal ranks and commercial coal seams used for pulverized coal (PCs power generation in the US; and (3) included "future fuels" such as blends and beneficiated coals. Once selected fresh coal samples were acquired and distributed to team members. These samples were subjected to ultimate, proximate, and ASTM ash analysis. Coal samples were analyzed for trace element concentrations by INAA at the MIT Nuclear Reactor Laboratory (Task 5).

Advanced analytical techniques such as Mössbauer spectroscopy and CCSEM are being used by UKy (Task 3) to determine the major mineral species present in the program coals and the combustion generated ash. This analysis provides important insight on the minerals present in the coal, how they interact during the combustion process, and how this interaction may affect the partitioning of toxic elements.

Another important issue is the form-of-occurrence of the trace elements in the coal. In this task the mode of occurrence of As, Cr, and Se is being determined by combining XAFS and the Mössbauer/CCSEM derived data discussed above. Hg will also be evaluated. Other less

critical trace elements (Mn, Ni, Zn, Pb, U, etc.) may also be evaluated, especially if their abundance is unusually high in any of the program coals. In addition, the form-of-occurrence of Cl and S in coals and chars will be investigated.

As a complement to the time-intensive XAFS analysis mentioned above, a unique protocol developed by USGS is being used in Task 4 to analyze selected raw coal, and size and density segregated coal, samples for trace element forms of occurrence. This protocol combines low temperature (< 200°C) ashing, chemical analysis, x-ray diffraction, coal segregation via flotation, ammonium acetate and selected acid leaching, electron microbeam measurements, and low and moderate temperature heating tests to determine the forms of elements in coal. Because of the unique combination of existing testing and analytical facilities available at USGS, the work is being conducted at USGS laboratories. In addition, a relatively new technique, synchrotron radiation x-ray fluorescence microscopy (SRXFM), available at the National Synchrotron Light Source, will be tested for application in this area by UKy (Task 3). This technique uses x-ray fluorescence excited by a focussed synchrotron x-ray beam for imaging and compositional analysis. The x-ray yield obtained from a given element is orders of magnitude greater than that possible in an electron microscope or microprobe; hence, its sensitivity to trace element modes is much better, particularly for modes of occurrence involving highly dispersed elements

*Combustion Zone Transformations*

The effect of coal type and combustion conditions on the emission of the toxic trace elements is being investigated using the MIT laminar-flow drop tube reactor (Task 5). The fundamental mechanisms of toxic species formation and partitioning will be determined from careful examination of the ash formed under a variety of combustion conditions. Measurements of the partitioning of the trace elements in the four coals as a function of temperature and equivalence ratio are underway. These measurements will provide the baseline data on the fraction vaporized for the different elements to be studied in greater detail in Phase II of the program. Individual size-segregated ash samples (collected with a cascade impactor) are then analyzed by INAA for total composition, Auger and STEM for surface composition, TEM and SEM for particle morphology, and possibly water washing and/or chemical leaching to determine the solubility of selected trace elements in the ash samples. Samples are also be submitted to UKy for chemical species analysis by XAFS and other techniques.

PSI will be performing a detailed experimental study to determine the fundamental behavior of toxic species during combustion, including low $NO_x$ conditions (Task 8). The work utilizes the PSI EFR that has been used in many previous combustion studies on mineral matter transformations during pc combustion. This reactor is on a scale intermediate between the bench top apparatus to be used by other team members (UA, MIT) and the UA laboratory-scale combustor. Therefore the combustor yields a better understanding of the overall behavior of toxic species while avoiding some of the confounding influences related to self-sustained combustion in the larger furnace. Utility-grind samples of the program coals are combusted under three different stoichiometric ratios, and two temperatures. Size segregated ash samples, and carbon filter samples will be collected. Ash samples collected during the combustion experiments are analyzed by INAA and other techniques at MIT. By performing an elemental

analysis on the size classified ash samples, we can identify the major mechanisms (e.g., vaporization and condensation) that govern the behavior of specific toxic species during the combustion process -- especially under reducing conditions.

*Post-Combustion Transformations*

The goal of this task is an increased understanding of the transformations of selected metals as the flue gases cool following the high temperature combustion zone. Experiments will be performed on two very different scales at UA. In addition, PSI will perform thermodynamic equilibrium calculations and make measurements of submicron aerosol size and composition from the large self-sustained combustor (Tasks 8 and 9).

At the small scale, UA will conduct experiments to explore the fundamental kinetics and mechanisms for metal vaporization and metal vapor-mineral interactions. Metal vapor-mineral interactions will be studied in this task using thermogravimetric analysis (TGA). The primary experimental parameters to be studied are temperature, gas composition (particularly the concentration of the metal species in the gas phase), the composition of the sorbent (char, silica, alumino-silicate, etc.), sorbent particle size and porosity, and exposure time (residence time). The primary properties that will be analyzed are the concentration of toxic trace metals in the particles as functions of time, the final chemical form of the trace metal, the leachability of the trace metal in the final particles, and if possible, the distribution of metal in the particles.

On a larger scale, UA will determine how both coal composition, detailed mineralogy and combustion conditions (including low $NO_x$ conditions) govern the fate of toxic metals under practical time/temperature, self sustained, yet still aerodynamically well defined, pulverized coal combustion conditions. Other tasks focus, one at a time, on individual aspects of toxic metal partitioning. In this task, experiments are performed with time-temperature profiles similar to those in pc combustors. Therefore, the hypothesis derived from the smaller scale facilities can be tested under 'real world' conditions to determine the dominant mechanisms for trace element partitioning. Results from this portion of the project, together with the other portions, will lead to a quantitative model that will predict the fate of all toxic species as functions of coal quality and combustion configurations.

Select coals will be burned in the UA self-sustained combustor under premixed conditions where all the coal is mixed with all the air prior to combustion. The baseline tests will employ the naturally occurring temperature profile for each coal at a stoichiometric ratio of 1.2. Samples will be withdrawn at the exhaust port. Complete impactor samples will be collected and analyzed for each toxic metal (11 as listed in the CAAA plus U and Th) plus major elements. This will yield the particle size segregated toxic metal composition, which can be compared to data obtained form other tasks of this program. This data will then be examined to determine particle size dependence in order to infer possible mechanisms governing the fate of each metal.

*Organic Emissions*

Some organic emissions associated with coal combustors can have deleterious effects on the environment and/or human health. It is therefore very important (1) to know the identities, quantities, and toxicities of the organic species released from coal combustion systems, and (2) to understand the chemical and physical processes that govern these species' formation, destruction, and release. Organic emissions data from the DOE Air Toxics and EPRI PISCES programs have the potential of benefitting the evaluation of the problem of organic emissions from coal combustion. In Task 7, Princeton University is conducting a critical review of the available field data, focusing on (1) the appropriateness, thoroughness, and reliability of the experimental techniques employed; (2) comparison with previously published emissions data; (3) the implications of the results; (4) similarly evaluating comparable data available from other countries, particularly Europe and Australia; reviewing emerging technical literature on coal pyrolysis and combustion processes that affect organic emissions; (5) staying abreast of new results in the toxicity literature, relating to organic emissions from coal; and (6) communicating regularly with the other principal investigators of the air toxics team so that all will be cognizant of the ties between the organic and inorganic air toxics issues.

It is expected that the above efforts of analysis and literature review will lead to (1) comprehensive understanding of what is currently known about organic emissions from coal and (2) identification of the important questions that may still need to be addressed in future research.

*Model Validation*

Also under Task 7, the University of Connecticut is conducting a preliminary review of the relevant field data on inorganic emissions. In Phase I we will use the field data to focus the experimental program and to validate the models we will develop in Phase II. The Phase I effort focuses on data from the following sources:

— EPRI PISCES
— DOE Program
— VTT (Finland)
— KEMA (Netherlands)

Important issues to be addressed when reviewing these data include mass balance closure, methods of analysis and sample collection, effect of APCD, effect of bulk coal ash chemistry, particle size distribution, and speciation of Hg.

*Model Development*

PSI will use its silicate equilibrium model accounts for the *non-ideal* behavior of multi component silicate solutions in combination with its trace element database to calculate Cr and As partitioning. These results will be compared with laboratory data generated under Tasks 5.1, 6.1, 6.2, and 8, and inorganic species field data reviewed as part of Task 7. These calculations may be repeated for Se and/or other elements if experimental data warrant interpretation of vaporization under conditions where silicate chemistry is dominant.

# SECTION 3

# RESULTS AND DISCUSSION

# 3. RESULTS AND DISCUSSION

## 3.1    Program Management (PSI)

During the last quarter the final program coal was procured and distributed to the team members. The coal, from the Wyodak seam in the Powder River Basin, was procured through a collaboration with another DOE-funded program at ABB. As with the program coals distributed earlier, all samples are stored under argon to prevent oxidation.

## 3.2    Coal Characterization (UKy, USGS, PSI)

In the last quarter work continued on the characterization of the program coals, and the forms of occurrence of trace elements in these coals. Characterization of the Wyodak began late in the quarter. The standard coal analyses, Ultimate, Proximate, and Ash Chemistry, were completed for this coal and are presented in the following subsections. Characterization by more advanced techniques such as XAFS, CCSEM, and the USGS leaching protocol is underway. Much of the coal and trace element information for the Pittsburgh, Elkhorn/Hazard, and Illinois No. 6 coals was presented in the last Quarterly Report.[2] Additional data on trace element forms of occurrence in these coals was obtained by both the USGS (leaching analysis) and the UKy group (XAFS analysis). These data are presented below.

### 3.2.1    *Ultimate, Proximate, and Ash Chemistry for Program Coals*

The results of Ultimate, Proximate, and Ash Chemistry analysis for the four program coals is shown in Table 3-1. As can be seen from this table the ash content for the Wyodak coal is similar to the other program coals. The moisture content is much higher for this coal than the bituminous coals. Moisture in the raw, crushed, coal obtained by ABB was much higher, approximately 30%. The drop in moisture content indicates that the coal was dried during pulverization at ABB. Another parameter that is much different than the bituminous coals is the high calcium content of the Wyodak coal. This high calcium content, and low iron content, is typical of coals from the Powder River Basin. Experiments with this coal will provide valuable insight on the role of calcium on arsenic retention in the fly ash.

### 3.2.2    *Trace Element Forms of Occurrence in Coal - New Data*

As part of this program a wide array of analytical techniques and procedures are being utilized to determine the mode of occurrence of selected trace elements in coal. By utilizing complimentary analytical techniques we can determine both the physical association of the trace element (e.g., mineral or organically associated) *and* the chemical speciation (e.g., oxidation state) of the trace element in the coal.

During the last quarter data from the sequential leaching tests performed earlier in the program were obtained by the USGS. These sequential leaching tests utilized a procedure similar to that described by Palmer et al.[3] which was modified from Finkelman et al.[4] Duplicate 5 g samples were sequentially leached with 35 ml each of 1N ammonium acetate ($CH_3COONH_3$),

Table 3-1. Coal Properties for Program Coals

| | Elkhorn/Hazard | | Pittsburgh | | Illinois No. 6 | | Wyodak | |
|---|---|---|---|---|---|---|---|---|
| | Dry Basis | As Received | Dry Basis | As Received | Dry Basis | As Received | Dry Basis | As Received |
| **Proximate (wt %):** | | | | | | | | |
| Fixed Carbon | 57.80 | 56.46 | 62.23 | 61.99 | 54.98 | 53.16 | 49.62 | 43.14 |
| Volatile Matter | 34.61 | 33.80 | 30.66 | 30.22 | 34.41 | 33.27 | 41.91 | 36.44 |
| Moisture | 0.00 | 2.33 | 0.00 | 1.44 | 0.00 | 3.31 | 0.00 | 13.06 |
| Ash | 7.59 | 7.41 | 7.11 | 7.01 | 10.61 | 10.26 | 8.47 | 7.36 |
| **Ultimate (wt %):** | | | | | | | | |
| Carbon | 76.66 | 74.87 | 77.74 | 76.62 | 70.02 | 67.70 | 61.19 | 53.20 |
| Hydrogen | 4.70 | 4.59 | 4.87 | 4.80 | 4.89 | 4.73 | 5.28 | 4.59 |
| Nitrogen | 1.46 | 1.43 | 1.50 | 1.48 | 1.22 | 1.18 | 0.95 | 0.83 |
| Sulfur | 0.84 | 0.82 | 1.66 | 1.64 | 3.72 | 3.60 | 0.25 | 0.22 |
| Oxygen | 8.58 | 8.38 | 7.01 | 6.91 | 9.50 | 9.20 | 23.86 | 20.74 |
| Chlorine | 0.17 | 0.17 | 0.099 | 0.098 | 0.035 | 0.034 | ** | ** |
| Moisture | 0.00 | 2.33 | 0.00 | 1.44 | 0.00 | 3.31 | 0.00 | 13.06 |
| Ash | 7.59 | 7.41 | 7.11 | 7.01 | 10.61 | 10.26 | 8.47 | 7.36 |
| **Ash Composition (wt %):** | | | | | | | | |
| $SiO_2$ | 55.83 | | 42.92 | | 44.38 | | 31.76 | |
| $Al_2O_3$ | 34.27 | | 22.87 | | 17.35 | | 18.04 | |
| $Fe_2O_3$ | 5.18 | | 19.18 | | 19.80 | | 5.81 | |
| $TiO_2$ | 1.71 | | 1.08 | | 0.91 | | 1.80 | |
| CaO | 1.84 | | 4.51 | | 4.00 | | 24.35 | |
| MgO | 0.60 | | 0.97 | | 0.85 | | 2.61 | |
| $Na_2O$ | 0.32 | | 1.28 | | 0.63 | | 0.90 | |
| $K_2O$ | 1.53 | | 1.21 | | 1.80 | | 0.70 | |
| $SO_3$ | 1.45 | | 5.40 | | 4.62 | | 12.93 | |
| $P_2O_5$ | 0.23 | | 0.57 | | 0.12 | | 1.10 | |

3N hydrochloric acid (HCL), concentrated hydrofluoric acid (HF; 48%) and 2N (1:7) nitric acid (HNO₃) in 50 ml polypropylene tubes. Each tube was shaken for 18 h on a Burrell[a] wrist action shaker. Because of the formation of gas during some of the leaching procedures it was necessary to enclose each tube in two polyethylene bags, each closed with plastic coated wire straps that allow gas to escape but prevent the release of liquid. Approximately 0.5 g of residual solid was removed from each tube for instrumental neutron activation analysis (INAA). The solutions were saved for inductively coupled argon plasma (ICP) analysis. The leaching results for the trace elements are discussed individually below. The raw leaching data, including selected major elements, can be seen in the USGS progress report in Appendix A.

The group at UKy is using XAFS spectroscopy and Mössbauer spectroscopy to complement the USGS work, and to examine the mode of occurrence of key HAPs and other elements in program coals. As discussed in the first Quarterly Report,[5] the XAFS spectra of the HAPs elements are obtained not just from the raw coal (RAW), but also from three fractions: (1) an "organic-rich" fraction (ORG) - either the fraction that floats in a 1.62 specific gravity liquid or the clean product from a Denver (froth flotation) cell; (2) a "heavy-minerals-rich" fraction (HYM) - the fraction of the refuse or tailings fraction from (1) that sinks in a 2.875 specific-gravity liquid; and (3) a "clay-rich" fraction (CLAY) - the float fraction from the 2.875 specific-gravity liquid. These fractions are then taken to the synchrotron for XAFS analysis. It should be noted that the approximate weight ratios of the different fractions separated from these coals according to this scheme are estimated to be: ORG:CLAY:HYM = >90%:5 to10%:<1%, depending on ash content. During the last quarter, new XANES data were obtained at Stanford Synchrotron Radiation Laboratory (SSRL), Palo Alto, CA, on Se and Zn in the program coals and the float/sink fractions.

New data for the individual elements are discussed separately below.

**Arsenic:**

Leaching data for arsenic in three of the program coals can be seen in Table 3-2. Because arsenic in the Pittsburgh and Illinois No. 6 coals was leached primarily by nitric acid, we infer the association of arsenic with pyrite. The association of arsenic with pyrite in these coals was confirmed by microprobe analyses (see Appendix A). In the Elkhorn/Hazard coal, arsenic behaves in a manner similar to that of iron; that is, arsenic is leached primarily by hydrochloric acid. It is possible that pyrite grains with high concentrations of arsenic (approximately 2 wt %) in the Elkhorn/Hazard were more readily oxidized than grains with low concentrations of arsenic (100 ppm arsenic). However, the arsenic data are incomplete, as indicated by low total percentages for arsenic in the four leachates (about 40%) and additional data are needed before a definite determination can be made. Comparison of the XAFS data and the leaching results suggest that the unleached arsenic may be derived from fine pyrite grains included in the carbon matrix. The carbon matrix may serve to shield the pyrite grains from the leaching solutions. To

Table 3-2. Mean Percentages of Arsenic Leached (Error ±25%)[*]

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[a] Use of tradenames and trademarks in this publication is for descriptive purposes only and does not constitute endorsement by the U.S. Geological Survey.

| Coal | Percent Leached by Each Solution | | | | Percent Remaining |
|------|-------|-----|-----|------|-----------|
| | Am. Ac. | HCL | HF | HNO₃ | |
| Pittsburgh | 1 | 11 | 5 | 57 | 26 |
| Elkhorn/Hazard | 1 | 29 | 6 | 4 | 60 |
| Illinois No. 6 | 1 | 19 | 5 | 40 | 35 |

*All data are preliminary and subject to revision as new data become available.

test this conclusion, future work may involve the examination of solid residue from the nitric acid leach to determine if some of the arsenic was not leached.

**Selenium:**

As discussed in the last Quarterly Report,[2] the selenium contents of the Elkhorn/Hazard and Illinois #6 coals are relatively high (2 to 3 ppm), whereas the Se content of the Pittsburgh coal is less than 1 ppm. Based on these high concentrations, and on some favorable preliminary data obtained earlier on the Elkhorn/Hazard coal, it was felt that a detailed XANES examination of Se in the Illinois #6 and Elkhorn/Hazard coals would be worthwhile. No examination of Se in the Pittsburgh coal or its fractions has been attempted.

Selenium K-edge XANES data were collected at SSRL over the energy range from 100 eV below the Se K-edge at 12,658 eV to about 300 eV above the edge. The XANES spectra, prepared from the raw XAFS spectra, are shown as Figures 3-1 and 3-2 for the Pittsburgh and Elkhorn/Hazard coals and fractions, respectively. The Se XANES spectrum obtained for the Pittsburgh 2.88 sink fraction has the best signal/noise ratio of any of the spectra in Figures 3-1 and 3-2 and, furthermore, it strongly resembles the XANES spectrum from As in the same fraction. Hence, most, if not all, of the Se in this 2.88 fraction is present as Se anions substituting for sulfur in the pyrite structure, in similar fashion to As. The Se XANES spectra of the raw and 1.62 float fractions of the Illinois #6 coal, although much noisier than that of the 2.88 sink fraction, appear to be similar to that of the pyrite-rich fraction. However, there is the presence of a small peak at about 8 eV in these two fractions that complicates the comparison; this peak arises from selenate ($SeO_4^{2-}$) species and is not observable on the 2.88 sink fraction. Again, when we compare these observations on Se to the arsenic data for the same coal, we find the corresponding arsenate ($AsO_4^{3-}$) species present in the raw coal and float fractions, but absent from the 2.88 sink fraction. Hence, there is a strong correlation between the occurrence of As and Se in the Illinois #6 coal and both of these elements appear to be predominantly associated with pyrite.

The 2.88 sink fraction for Elkhorn/Hazard is similar to that observed for the Illinois #6 coal, and we conclude that most of the Se in this fraction is also associated with pyrite. However, because the spectrum is less defined than that of the Illinois #6 coal fraction, it is possible that other Se forms may also be contributing to this spectrum. In contrast to the Illinois #6 situation, the Se XANES of the column float fraction lacks any features that can be attributed to Se in pyrite. Furthermore there is a weak peak at about 18 eV, present also in the spectrum of
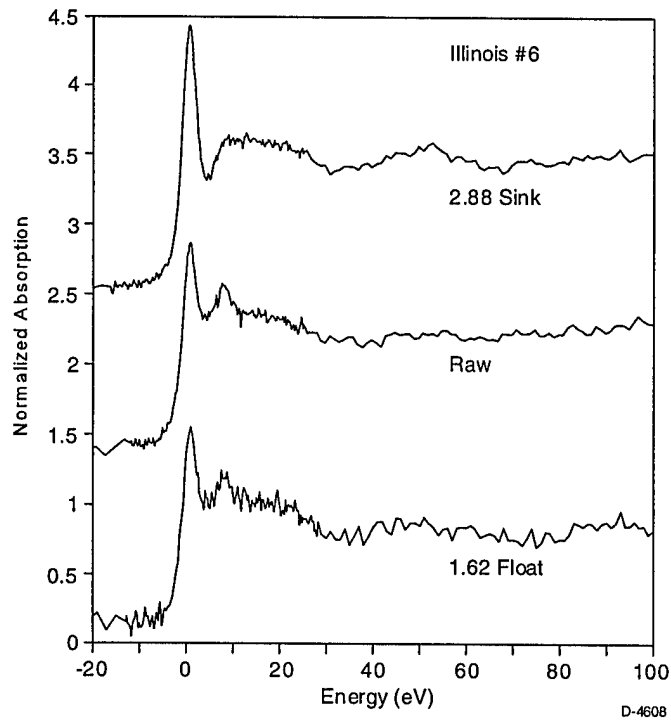
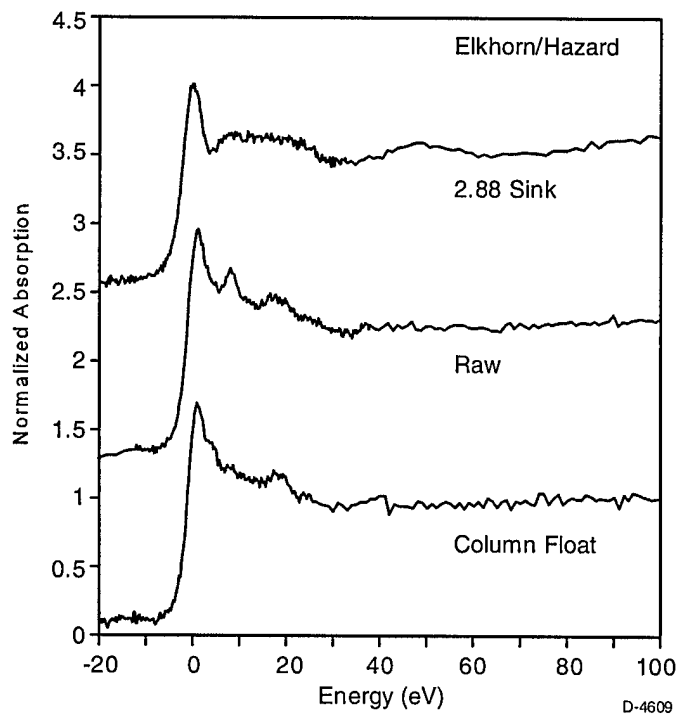Figure 3-1. Se XANES of raw Illinois No. 9 coal and float/sink fractions.



Figure 3-2. Se XANES of raw Elkhorn/Hazard coal and float/sink fractions.

the raw coal, that clearly must arise from another form of Se than Se in pyrite. We interpret this spectrum as arising from an organoselenium form in the column float fraction.

The data on relative step-heights (Table 3-3) are also quite revealing. In the case of As and Se in the Illinois #6 coal, there is a close correspondence between the step-heights for these two elements in the different fractions. For Elkhorn/Hazard, however, the As step-height data for the different fractions show more variation than the data for Se. This difference would also suggest that Se and As are not as closely associated in the Elkhorn/Hazard coal as appears to be the case for the Illinois #6 coal. Hence, we interpret these observations to indicate that in the Elkhorn/Hazard coal there is a significant selenium form that is not duplicated by arsenic and does not segregate between fractions. Again an organoselenium form is indicated. Owing to the small fraction of pyrite in the Elkhorn/Hazard coal, it is likely that the organoselenium form is the major form of Se in this coal since the Se step-height for the pyrite fraction is only 2.5 times that of the float fraction.

Table 3-3.  Comparison of As and Se Step-Heights and wt % Pyritic Sulfur for Elkhorn/Hazard and Illinois #6 Coals

| Coal Sample Fraction | Arsenic Step-Height | Selenium Step-Height | wt % S as Pyritic |
|---|---|---|---|
| Elkhorn/Hazard ORG | 0.6 | 0.9 | 0.12 |
| RAW | 1.0 | 1.0 | 0.15 |
| CLAY | 2.1 | -- | 0.40 |
| HYM | 4.0 | 2.0 | 12.6 |
| Illinois #6 ORG | 0.75 | 0.8 | 0.71 |
| RAW | 1.0 | 1.0 | 1.45 |
| CLAY | 4.0 | -- | 9.60 |
| HYM | 6.0 | 5.0 | 34.0 |

**Zinc:**

Although zinc is not one of the HAP elements listed in the 1990 Clean Air Act Amendments, a brief investigation into the mode of occurrence of zinc in the program coals has been undertaken because of the high concentration of zinc, approximately 70 ppm, in the Illinois #6 coal, and also because experiments carried out at MIT, reported in the last Quarterly Report,[2] indicated the vaporization behavior of zinc to be somewhat variable among the three coals.

Zinc XANES spectra were obtained for all three coals and for the float/sink fractions from the Illinois #6 coal. The zinc XANES for the Illinois #6 coal and fractions are shown in Figure 3-3. These spectra show significant variation, particularly for the two extreme fractions,
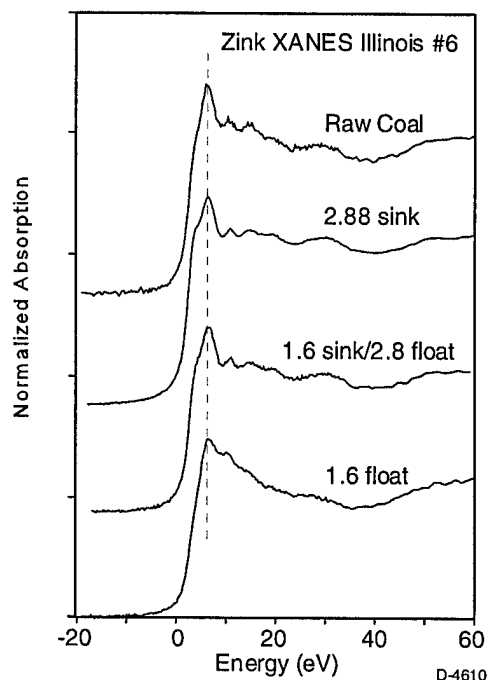
Figure 3-3. Zn XANES of raw Illinois No. 9 coal and float/sink fractions.

the 2.88 sink and 1.62 float. The spectrum of the 2.88 sink fraction can be readily identified as arising from sphalerite, $ZnS$; this should be no surprise because zinc-bearing minerals, especially sulfides, are well known to be a characteristic feature of coal seams from Illinois. However, it is clear from the spectra in Figure 3-3 that not all of the zinc in this sample of Illinois #6 coal is present in this form. In particular, the Zn XANES spectrum of the 1.62 float fraction is significantly different, while the spectra of the intermediate fraction (1.6 sink/2.88 float) and raw coal appear to be composites of the two extreme spectra. At this time, it is not clear what the dominant form of zinc present in the float fraction might be.

A comparison of the zinc XANES spectra of the three coals is shown in Figure 3-4. Whereas the spectrum of the Illinois #6 coal appears to be dominated by Zn in the form of $ZnS$, it is clear that $ZnS$ is not present to any significant degree in the other two coals. Again, although the precise form of zinc in these other two coals is not apparent at this time, it is possible that the zinc may be in oxygen coordination based on the shift of the main peak.

3.3    Combustion Zone Transformations (PSI, MIT, UKy)

Work on the transformations of trace elements in the combustion zone is proceeding along two major fronts. In the first area investigators at PSI and UKy are working to determine how the oxidation state of pyrite and arsenic influence trace element vaporization in the combustion zone. In the second area investigators at MIT are working with the size and density segregated coals and a droptube reactor to evaluate vaporization behavior of trace elements. This work is expanded upon at PSI where investigators at PSI are using the utility grind coal and the PSI EFR to determine the net vaporization of trace elements in the combustion zone.
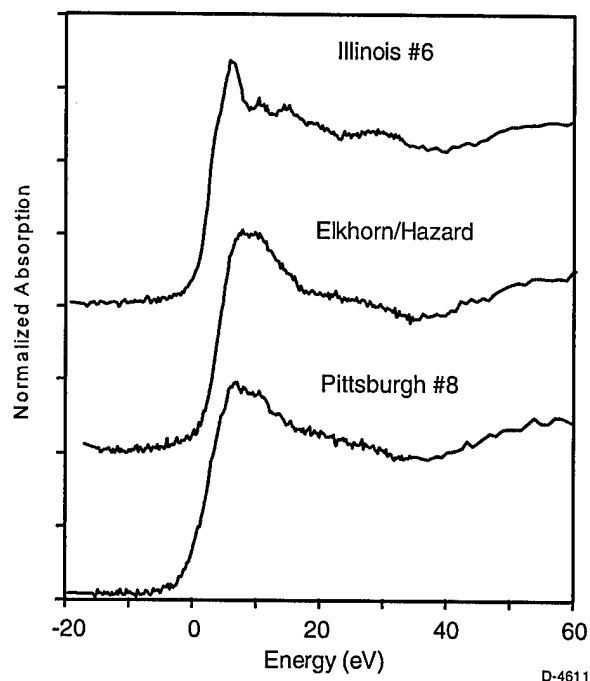
3-10

Figure 3-4. Zn XANES of raw Elkhorn/Hazard coal and float/sink fractions.

### 3.3.1  *The Effect of Coal Oxidation on Trace Element Vaporization in the Combustion Zone*

Arsenic has been reported to be quite variable in how it partitions between fly ash and bottom ash fractions in the combustion process and it has been proposed that it is the mode of occurrence of the arsenic in the coal that is the cause of the variability. As a result, at the Project Review meeting held in Pittsburgh in September 1996, it was agreed by researchers at PSI and at UKy to explore this question further. To do this, and to explore how pyrite oxidation may affect vaporization of other species commonly associated with pyrite (e.g., selenium), an experiment was designed to alter the oxidation state of the pyrite in the coal and then measure the vaporization of trace elements in the oxidized coal. Oxidation of the coal is currently underway at UKy by simulating natural weathering to oxidize the pyrite.

Three samples of approximately 1200 g of the Illinois #6 coal were laid out in trays. Two of the trays were placed in a laboratory oven at 50°C, while the third tray was located in a quiet corner of the laboratory at ambient conditions (20°C). A beaker of water was also placed in the oven to ensure a moist atmosphere. The beaker was periodically refilled until the coal was saturated. At that point the source of water was removed and the coal allowed to dry. After 60 days, a sample of the coal was taken from the oven and subjected to Mössbauer spectroscopy to determine the extent of oxidation of the iron. The Mössbauer spectrum is shown in Figure 3-5 and indicates, in comparison to data for the fresh coal reported in the last quarter's report, that about 50% of the iron has been oxidized. The main product is the ferrous sulfate szomolnokite ($FeSO_4.H_2O$) with a minor amount of jarosite formed as well. At 90 days, one tray will be removed and the coal will be shipped to PSI for combustion testing. A small sample will be retained at UKy for Mössbauer and XAFS determinations of the iron and arsenic oxidation states.
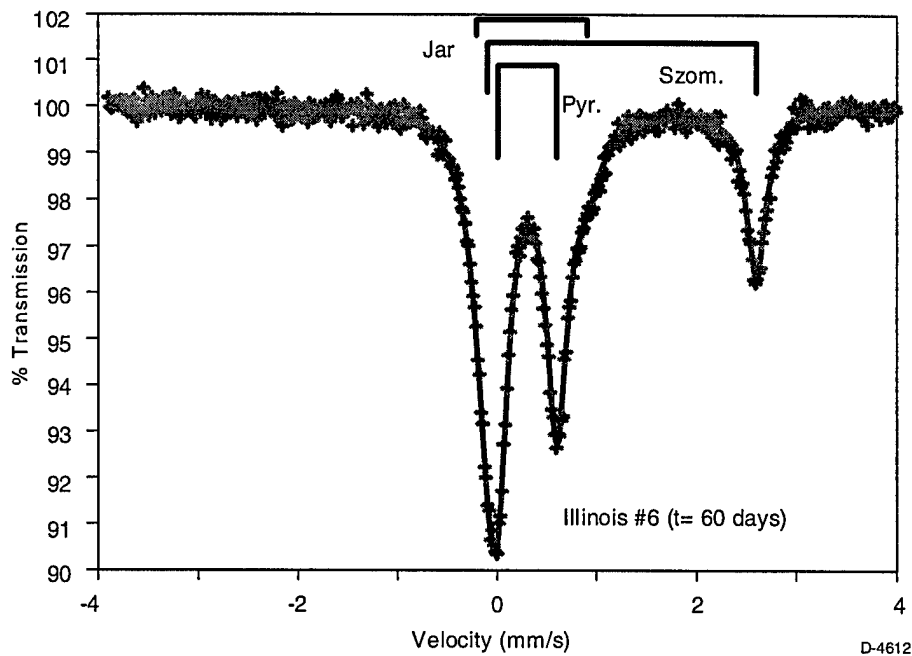
3-11

Figure 3-5. Mossbauer spectrum of Illinois No. 6 "weathered" for 60 days at 50°C.

### 3.3.2 *Trace Element Vaporization in the Combustion Zone*

During the last quarter baseline combustion experiments on the PSI EFR were completed for the three bituminous coals. The coals were combusted at a stoichiometric ratio of 1.2, with air as the combustion gas. The furnace setpoint was 1500°C, yielding a maximum gas temperature of 1450°C. Size segregated ash samples were collected with a water-cooled nitrogen quench probe and a cascade impactor. As can be seen from Figures 3-6 and 3-7 the ash particle size distribution from the Illinois No. 6 is slightly finer than the other two coals. The data in Figures 3-8 and 3-9 show that the ash generated from the Elkhorn/Hazard coal at fuel rich conditions was very similar in size to that generated under fuel lean conditions. A similar trend was noted for the Pittsburgh coal (Figures 3-10 and 3-11).

Based on INAA of the size segregated ash samples, it was possible to estimate the fractional vaporization of any given element, defined as the fraction of that element found in the submicron ash. Figure 3-12 shows the effect of combustion conditions on the trace element vaporization in the Elkhorn/Hazard coal. These data suggest that the combustion conditions, fuel rich or fuel lean, may play a major role in trace element vaporization. The reason for the decreased vaporization of all elements at lower stoichiometric ratios is unclear, but may include lower particle temperatures and increased oxidation times for inherent pyrite particles. If, as was suggested in the last Quarterly Report,[2] the vaporization of pyrite-associated species, such as arsenic, is linked to the oxidation of the pyrite, the lower oxidation of the pyrite would lead to the observed decrease. This trend is also seen in the data for the Pittsburgh coal. Figure 3-13 shows the effect of combustion conditions on trace element vaporization in the Pittsburgh coal. Data from a Pittsburgh coal in an earlier program (denoted as 1.2[*]) are also shown. It is interesting to note that the fractional vaporization under fuel lean conditions for both Pittsburgh coals is qualitatively similar.

3-12
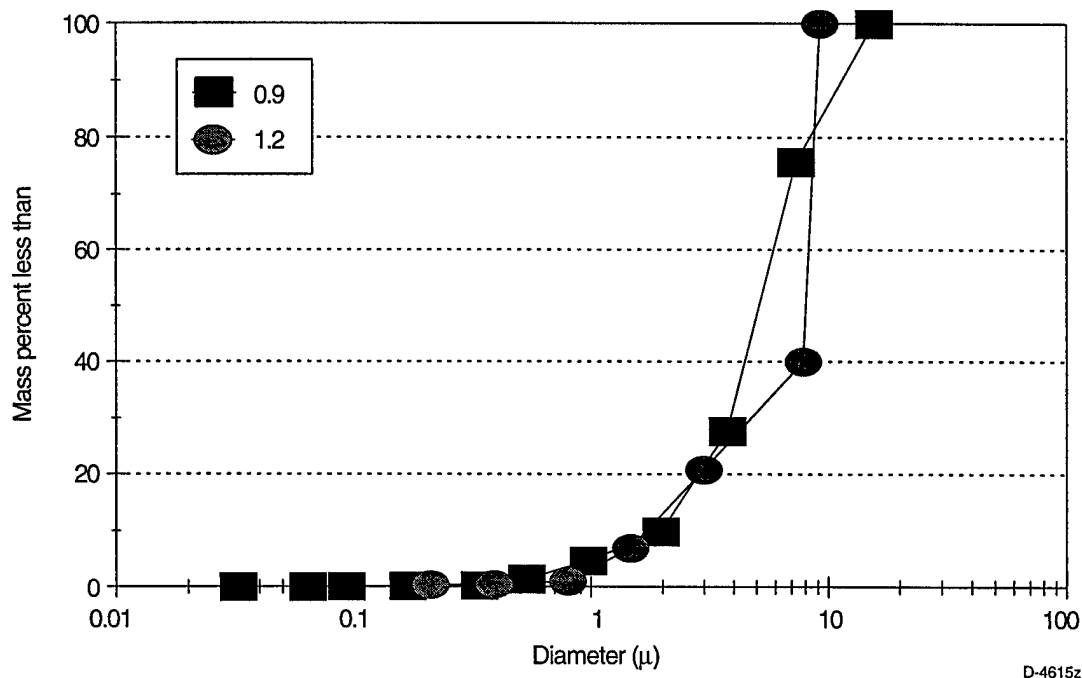
Figure 3-8.  Cumulative ash particle size distributions for Elkhorn/Hazard at different stoichiometric ratios (PSI EFR, 1.6 s residence time, 1500 °C).
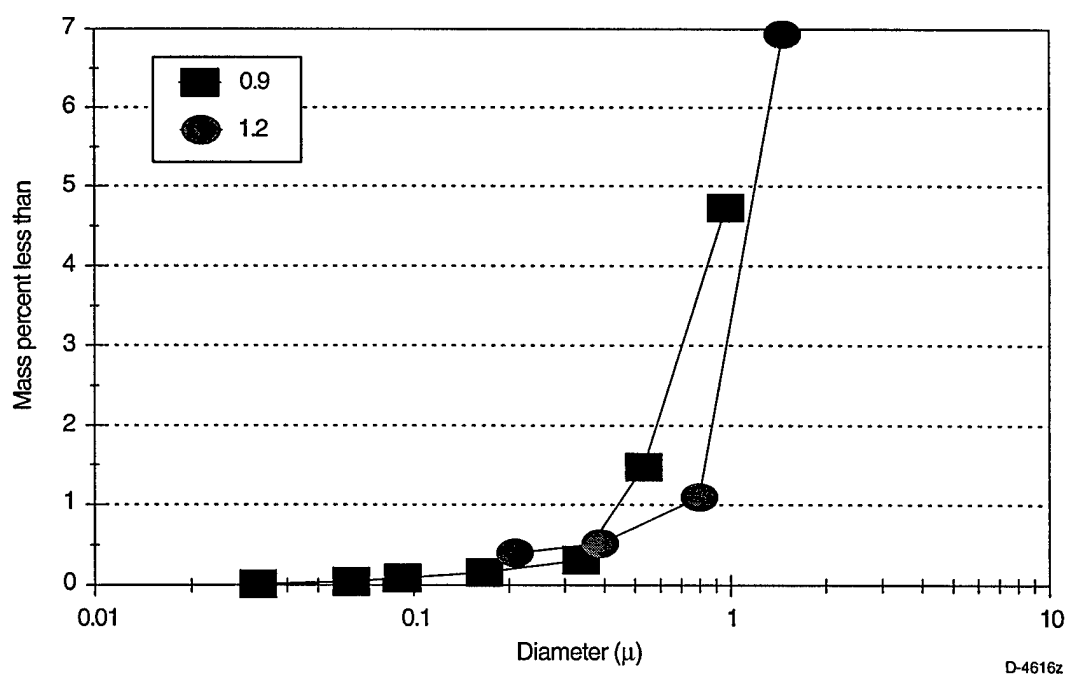


Figure 3-9.  Cumulative submicron ash particle size distributions for Elkhorn/Hazard at different stoichiometric ratios (PSI EFR, 1.6 s residence time, 1500 °C).
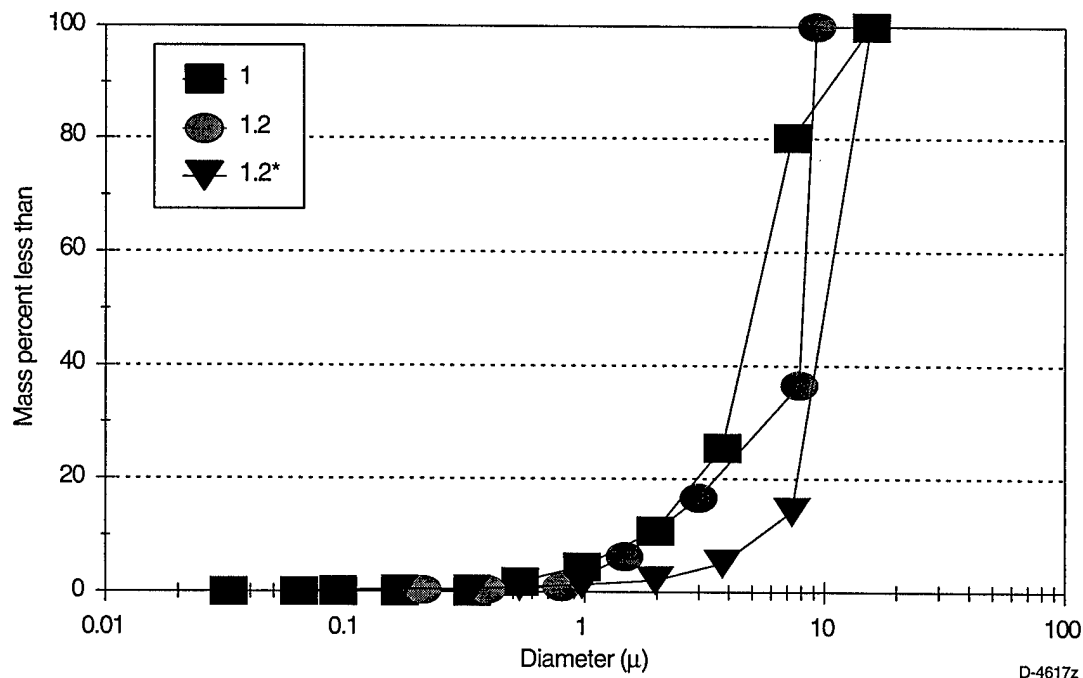
Figure 3-10. Cumulative ash particle size distributions for the Pittsburgh coal at different stoichiometric ratios (PSI EFR, 1.6 s residence time, 1500 °C).
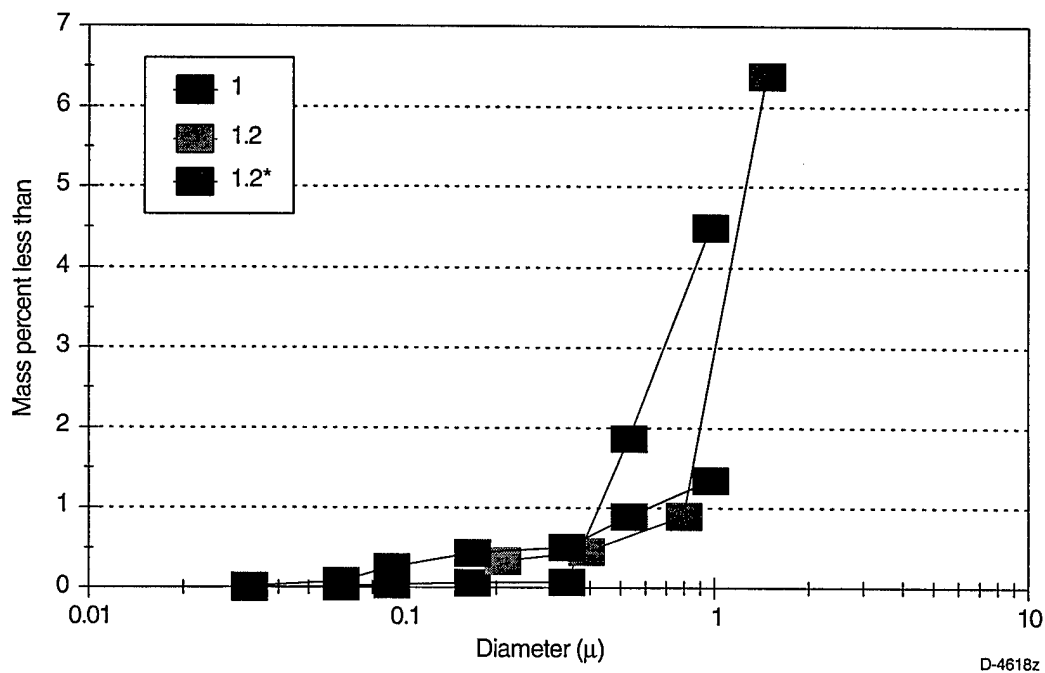


Figure 3-11. Cumulative submicron ash particle size distributions for the Pittsburgh coal at different stoichiometric ratios (PSI EFR, 1.6 s residence time, 1500 °C).
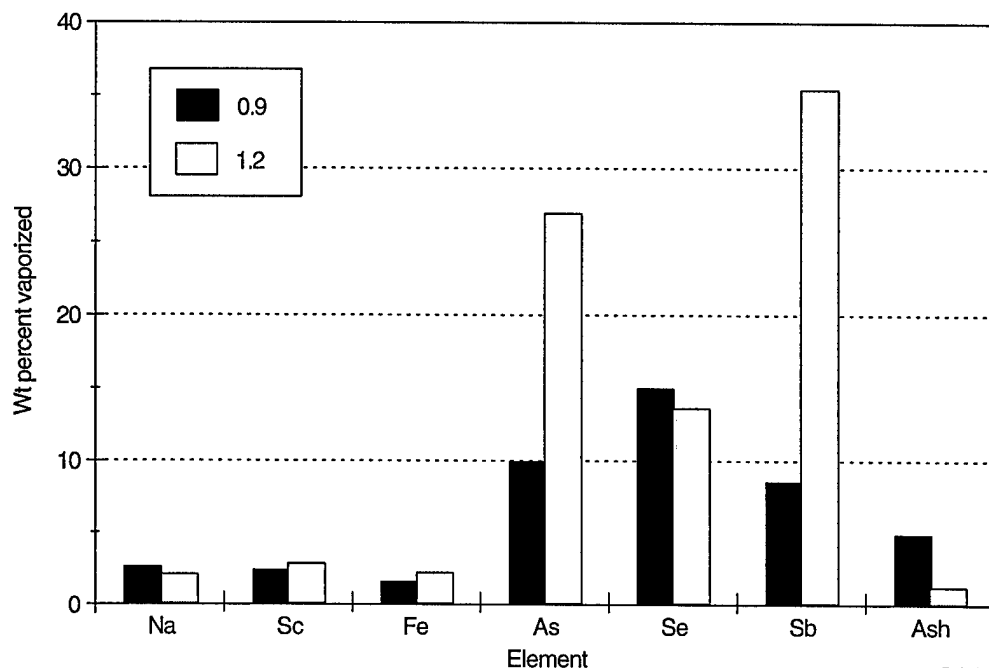
Figure 3-12. Fractional vaporization for several elements in the Elkhorn/Hazard coal at different stoichiometric ratios (PSI EFR, 1.6 s residence time, 1500°C).
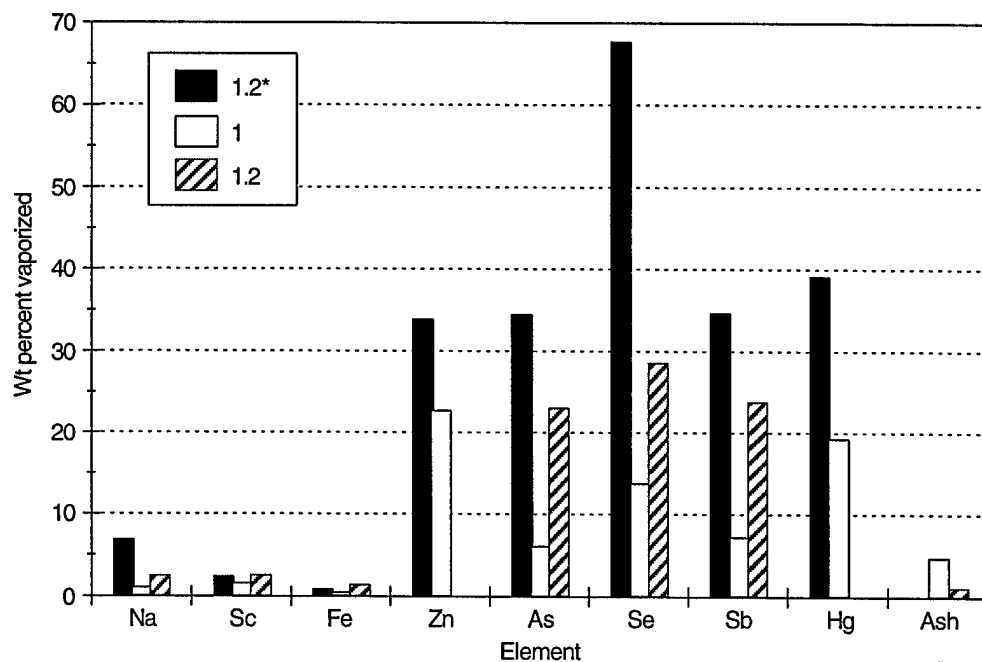


Figure 3-13. Fractional vaporization for several elements in the Elkhorn/Hazard coal at different stoichiometric ratios (PSI EFR, 1.6 s residence time, 1500°C).

Although these data qualitatively support the pyrite oxidation hypothesis, more data are required to better understand the effect of reducing conditions on trace element vaporization. Collection of these data at both PSI and MIT is underway.

Additional data on ash vaporization were obtained for density and size segregated samples of the Pittsburgh, Illinois #6, and Elkhorn/Hazard (referred to as KY on the figures) in the MIT drop tube furnace. The combustion conditions were selected to yield volatilization amounts comparable to those encountered in utility boilers. For a drop tube operated at 1700 K, the heat losses to the walls are larger than for the near adiabatic conditions in the center of a large scale boiler. In order to compensate for the effect of the radiative heat transfer to the walls on the particle combustion temperature, a value of 20% was selected for the oxygen concentration. These conditions had been previously used by Quann et al.[1] in a 20-coal study. The results from the previous study, while providing interesting trends on the extent of the vaporization and condensation of different elements, were for coals for which detailed mineral characterization was not available. The results of the present study will have the advantage of the detailed coal characterization to support the combustion studies. In this progress report the data from this study are compared with the Quann et al.[1] study in order to determine the effects of size and density segregation on vaporization behavior. The results for selected elements are presented below. For each element, the data on the amount of the element collected in the submicron aerosol is plotted on the ordinate, and the amount of the element in the coals plotted on the abscissa. A least mean square line fitted through the data gives a measure of the fraction of the element in the coal that is vaporized and recondensed.

**Arsenic:**

The results are all fitted by the same line with modest scatter (Figure 3-14). The fractional vaporization is 0.4. The points that depart significantly from the correlation are the low rank coals (MS, MR, WY) in the Quann et al.[1] study. In these coals there is opportunity for the vaporized arsenic to react with calcium oxide in the residual fly ash, thus reducing the amount that condenses in the submicron aerosol. This hypothesis will be tested when the low rank coal in the present study is burned.

**Zinc:**

The data in the Quann et al.[1] study (Figure 3-15) were correlated with two lines (fractional vaporizations of 0.06 and 0.26 ), one for the low rank and the other for the high rank coals. The data in the present study show the interesting anomaly that the result for the Elkhorn/Hazard coal (KY) are more consistent with the low rank coals in the Quann et al.[1] data than the bituminous coal. There is also an interesting size dependence of the vaporization of the zinc in the dense fraction of the Illinois coal.
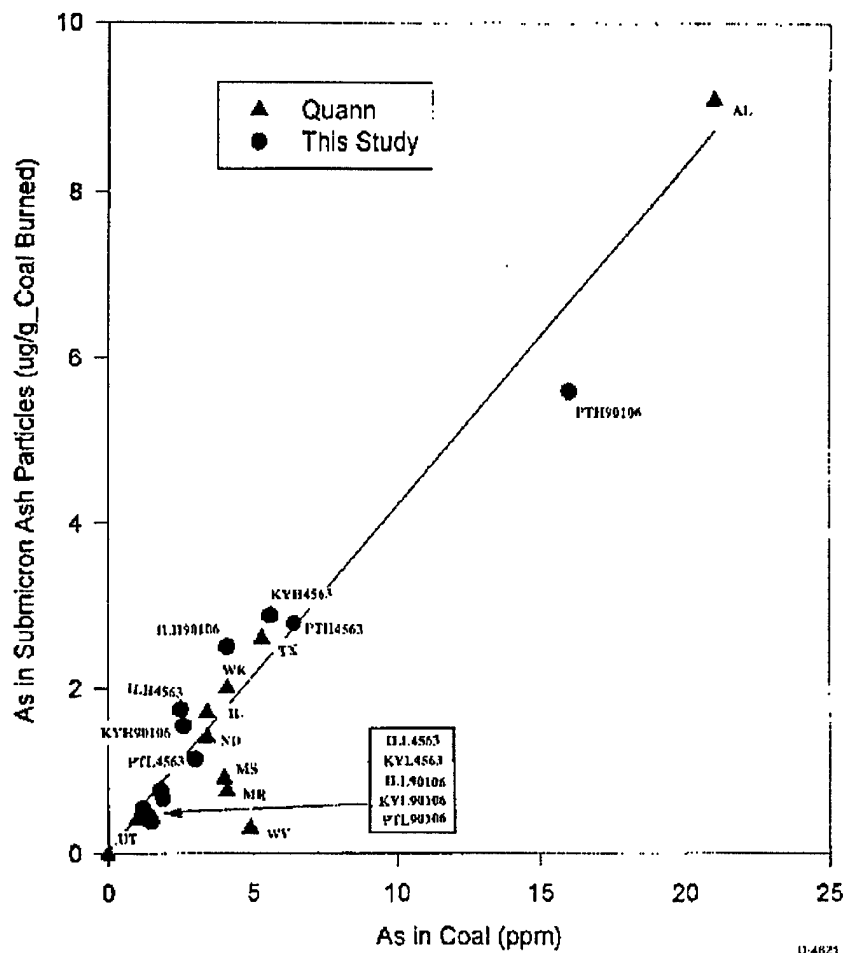
Figure 3-14. Effect of As concentration in coal on the total As collected in submicron ash.

## Iron:

The data for iron (Figure 3-16) show a much smaller vaporization than arsenic and zinc, with a fractional vaporization of 0.027. The points lying above the line are the low rank coals from the Quann et al.[1] study and the Elkhorn/Hazard (KY) coal from the present study. Again, the Elkhorn/Hazard coal shows a resembling that of a low rank instead of a high rank coal.

## Chromium:

The data show considerable scatter (Figure 3-17). Insights on the cause for this scatter may be obtained from the major differences seen with changing density for the 45/63 μm fractions for the Illinois No. 6 (IL), Pittsburgh (PT), and Elkhorn/Hazard (KY) coals.
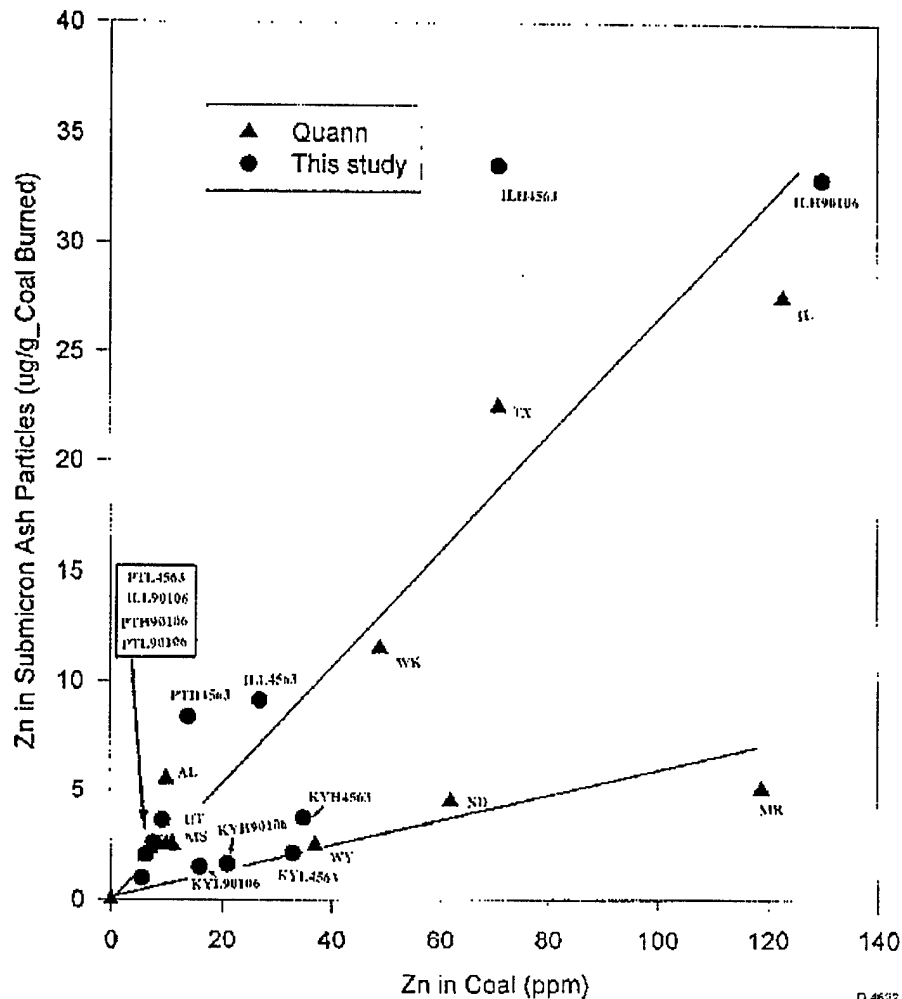
Figure 3-15. Effect of Zn concentration in coal on the total Zn collected in submicron ash.

**Sodium:**

For the present coal, the Pittsburgh and the Elkhorn/Hazard coals show lower vaporization than the Illinois No. 6 (Figure 3-18). There is also considerable scatter in the results of Quann et al.[1] which may be caused by the same inter-coal differences. One possible explanation for these differences may be difference in the extent of reaction between sodium and silica in the different coals. If this were the case, then the vaporization of the sodium for the lower rank coals should be higher than those for the higher rank coals. This seems to be the case. Knowledge of the size of the silica mineral inclusions is needed to be able to assess these effects. CCSEM data will be obtained for that purpose.
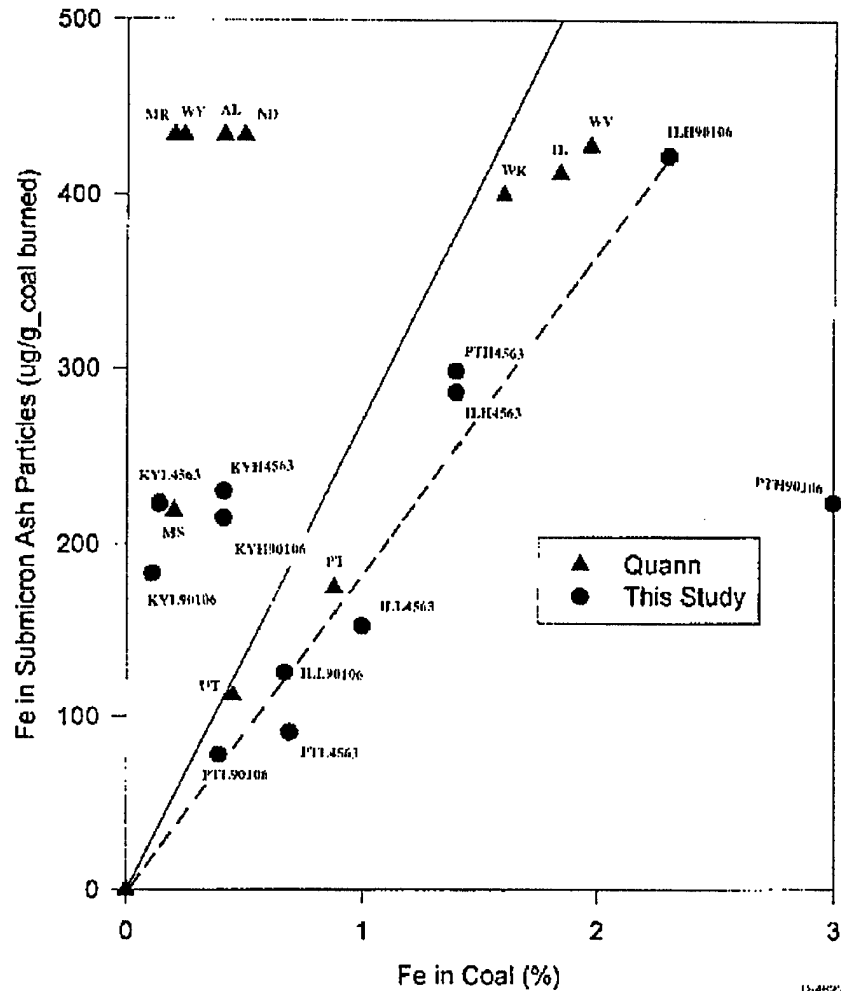
Figure 3-16. Effect of Fe concentration in coal on the total Fe collected in submicron ash.

**Mercury:**

The results on mercury are of interest in that they show high values of mercury capture by the ash, particularly for the Pittsbugh coal (Table 3-4). The mercury is captured primarily with the large, residual ash. It is probable that the mercury is captured with carbon, either char or soot, in the ash. The amount of carbon is relatively small based on measurement of weights of the residual ash which did not reveal the carbon within the uncertainty in the mass balance.

The results from this study will be used to guide the mineral characterization studies. For arsenic, the interest is in the size of calcium-rich inclusions in the coal. For sodium, it is the size of the silica inclusions. For mercury, separate runs will need to be made for purposes of obtaining carbon content. As more elements are analyzed, additional leads are expected to emerge.
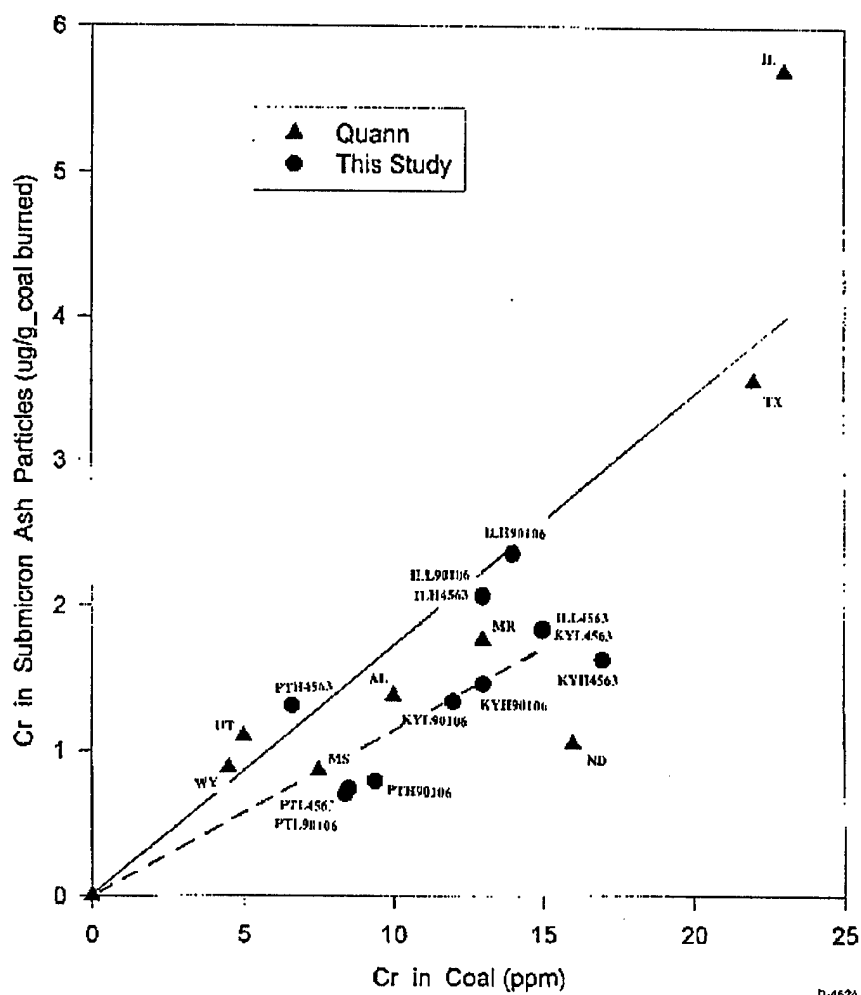
Figure 3-17. Effect of Cr concentration in coal on the total Cr collected in submicron ash.

Table 3-4. Hg Distribution in Ash Produced by Coal Combustion at $T_{furnace} = 1700$ K, $O_2 = 20\%$

| | Percentage in Larger Ash Particale (> 1 micron) ( %) | Percentage in Submicron Ash Particle (%) |
|---|---|---|
| KY H 4563 | 36 | 2.5 |
| KY L 4563 | 29 | 8.5 |
| KY H 90106 | 86 | 0.2 |
| KY L 90106 | 84 | 6 |
| PT H 4563 | 61 | 2.4 |
| PT L 4563 | 95.6 | 4.4 |
| PT H 90106 | 19 | 0.3 |
| PT L 90106 | 94 | 6 |
| IL H 4563 | 16 | 1.7 |
| IL L 4563 | 18 | 14.6 |

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| IL H 90106 | 13 | 0.7 |
| IL L 90106 | 21 | 3 |
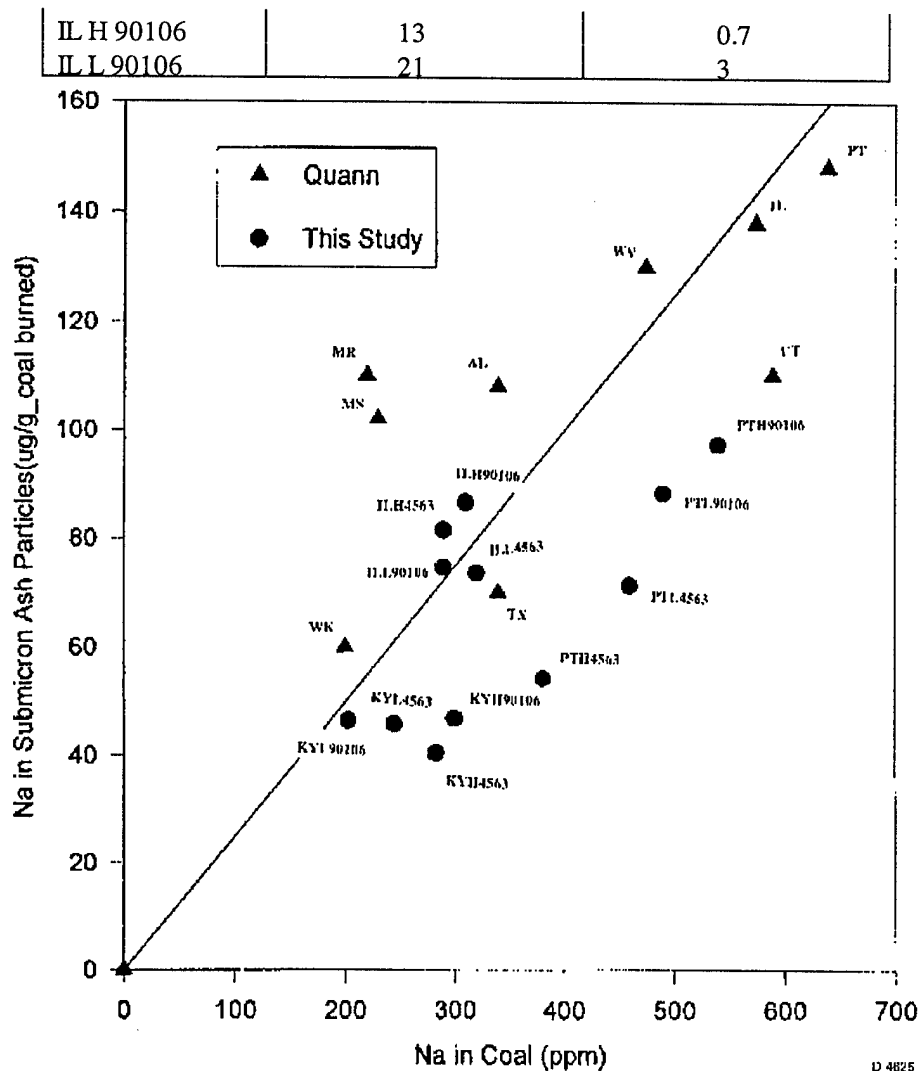


Figure 3-18. Effect of Na concentration in coal on the total Na collected in submicron ash.

## 3.4 Post-Combustion Transformations (UA, PSI, UKy)

Trace element transformations in the region between the furnace exit and the ESP play a critical role in determining the partitioning of that element between flyash captured in the ESP and vapors emitted from the stack. In this program we are investigating these post-combustion transformations on two different scales. Mercury capture by residual carbon, shown to be an important mechanism for mercury retention in the ash, is being evaluated in a small benchtop facility. Interactions, such as condensation and reactive scavenging, between vaporized species such as arsenic and selenium are being investigated using the larger self-sustained combustor at UA. Mercury speciation in flue gas is being evaluated in the PSI EFR.

### 3.4.1 Mercury Capture by Residual Carbon

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During the last quarter the PSI EFR was used to produce partially combusted chars from three of the program coals. The Elkhorn/Hazard, the Pittsburgh, and the Illinois No. 6 coals were all combusted at a stoichiometric ratio of 0.6, and a maximum gas temperature of 1450°C. The resulting chars were then sent to the UA for the mercury capture experiments. Because the presence of sulfur in activated carbon has been shown to affect mercury uptake, a small sample of the chars were sent to the UKy for XAFS analysis, and to a commercial laboratory for forms of sulfur analysis. The data from the commercial laboratory will be discussed in the next quarterly report.

Figure 3-19 shows the sulfur XANES spectra of char samples prepared from the project coals. These spectra are in the process of being analyzed according to least-squares fitting procedure developed for sulfur in coals and chars and only a preliminary semi-quantitative analysis will be presented here. Approximate estimates of the %S in different forms in the three chars are given in Table 3-5.
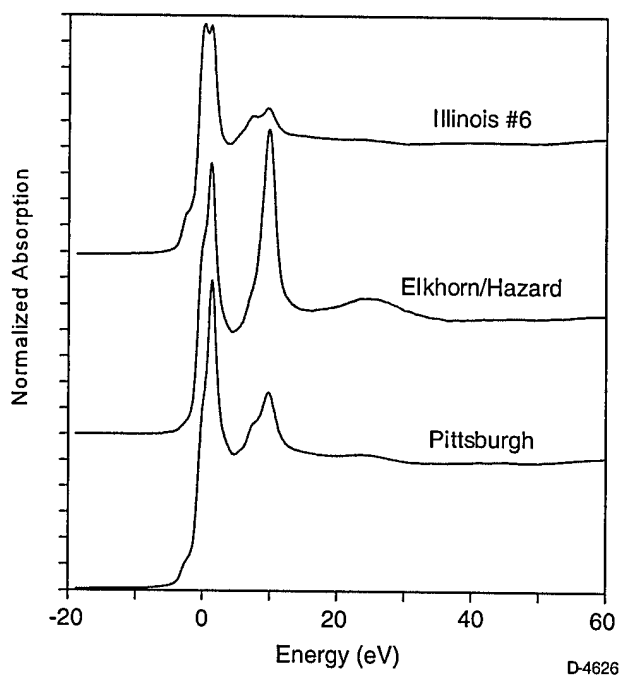


Figure 3-19. Sulfur XANES spectra of chars from three program coals.

Table 3-5. %S in Different Forms in Char Samples from Sulfur XANES Spectroscopy

| Sulfur Form | Elkhorn/Hazard | | Pittsburgh | | Illinois #6 | |
|---|---|---|---|---|---|---|
| | P in eV | %S | P in eV | %S | P in eV | %S |
| Pyrrhotite | -- | <5 | -2.2 | 20 | -2.2 | 35 |
| Elemental Sulfur | 0.1 | 30 | 0.0 | 25 | 0.1 | 35 |
| Organic Sulfide | 1.5 | 42 | 1.5 | 50 | 1.5 | 29 |
| Sulfate | 10.1 | 25 | 9.9 | 5 | 9.8 | 2 |

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| Other | -- | <3 | -- | -- | -- | -- |
|-------|----|----|----|----|----|----|

The prominent shoulder at about -2.2 eV in the Pittsburgh and Illinois #6 samples is due to pyrrhotite, whereas the second shoulder at about 0.0 eV in Elkhorn/Hazard and Pittsburgh coals and the peak at 0.0 eV in Illinois #6 coal is due to elemental sulfur. The sulfate peak at around 10 eV for the Elkhorn/Hazard coal is much larger than those for the Illinois and Pittsburgh coals. The spectra indicate that pyrite in the coal has decomposed to a mixture of pyrrhotite ($Fe_{1-x}S$) and elemental sulfur. Interestingly, the %S in the form of pyrrhotite and elemental sulfur are approximately the same for the Illinois #6 and Pittsburgh coals, whereas the elemental sulfur is much higher than the pyrrhotitic sulfur for the Elkhorn/Hazard coal. However, it should be noted that the %S as sulfate is almost the same as the %S as elemental sulfur for this coal, suggesting, perhaps, that the lack of observation of pyrrhotite is because the pyrite or the pyrrhotite has oxidized to sulfate, either during or prior to the char formation from the Elkhorn/Hazard coal. Whether this difference reflects the lower iron content of this coal or the fact that the Elkhorn/Hazard coal is more highly oxidized than the other two coals has yet to be resolved. Also, it should be recalled that sulfur can also escape from the coal during char formation and, therefore, a more detailed analysis must await a determination of total sulfur in these char samples.

While the chars were being prepared and characterized, work continued on the experimental apparatus and procedure for the mercury capture experiments. A schematic diagram of the experimental apparatus is given in Figure 3-20. The gas preparation section consists of gas sources (1) and a water saturator (2). This section is designed to deliver a simulated flue gas with a composition of 80% nitrogen, 15% carbon dioxide, 3% water vapor, and 2% oxygen. The gas flow rates are measured and monitored by three mass flow controllers to control the nitrogen,



Figure 3-20.  Schematic of reactor for mercury capture experiments; (1) gasses, (2) water saturator, (3) reactor, (4) constant temperature controller.
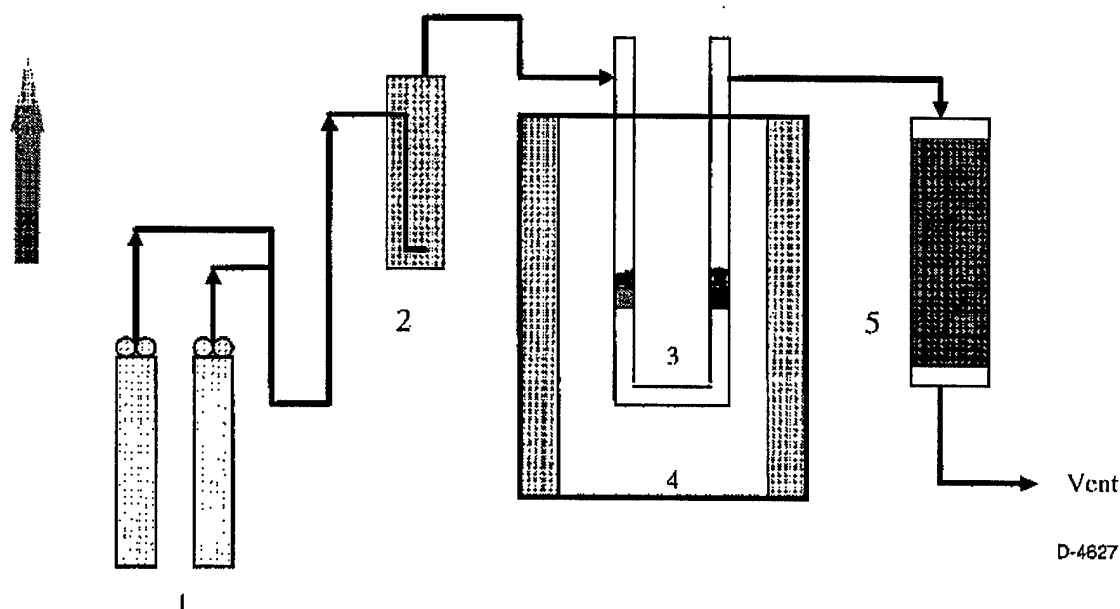
carbon dioxide, and air. These flow controllers are calibrated with standard calibration gases. The reactor section consists of a reactor (3) and a heating source whose temperature is controlled by a constant temperature controller (4). The reactor is a U-shaped tube. Mercury is placed into the left side of the U-shaped reactor and the mercury vapor generated is brought by the simulated flue gas into the right side of the reactor where the sorbent is placed. The required reactor temperatures are obtained by placing them into well controlled heat sources. The temperature of the mercury source and the temperature of the sorbent can be controlled independently. The last section consists of two activated carbon columns placed in series to ensure complete removal of mercury before venting to the atmosphere for the safety and environmental concerns.

During the experiments the desired temperature are achieved by setting and adjusting the constant temperature controllers. Both temperatures are held constant during the period of experiment. Once the temperatures are constant, the simulated flow gas (SFG) is introduced by the gas preparation section. The mercury source is then placed into an glass basket, which is then put into the source reactor. The mercury is vaporized inside the source reactor and the vaporized mercury is then carried away by the SFG into to the sorbent reactor. The sorbent to be tested (partially combusted char) is placed in the sorbent reactor on an distribution bed. The sorption begins when the mercury containing SFG flow through the reactor. The SFG then flows through the carbon traps to remove the remaining mercury vapor before the gas is exhausted to the atmosphere.

The concentration of mercury in the gas phase is extremely important, and will be calibrated by two methods. One is the direct weighting method. The weights of the mercury source before and after each experiment are measured by a analytical balance up to four digital accuracy. The gas concentration is then calculated by using the weight difference and the gas flow rate. The second method is using atomic adsorption. This is done by a blank run with only source in the source reactor while keeping the other conditions the same with experimental conditions. The vaporized mercury is then condensed or captured totally by a downstream device. The captured mercury is then analyzed by atomic adsorption to determine the mercury concentration. The concentration of mercury in the reactant is determined by cold vapor atomic adsorption spectroscopy. The data are used to determine the sorption ability and capacity of sorbent.

The planned experimental conditions are as follows:

| | |
|---|---|
| Mercury source temperature: | 70°C |
| Sorbent reaction temperature: | 70 and 160°C |
| Flow rate: | 100 scc/min |
| Gas composition: | SFG |

### 3.4.2  *Forms of Mercury Captured by Residual Carbon*

Given the importance of residual carbon on mercury retention in fly ash, it is important to get a better understanding of the forms of mercury present in the char. Through an arrangement

between the DOE Project Manager of closely allied DOE research projects (T. Brown) and the Principal Investigators on these programs, char and ash samples were received from Radian International and from the Energy and Environmental Research Center at the University of North Dakota (UNDEERC) that had been exposed to a simulated flue gas containing elemental mercury. The objective was to identify the forms of mercury and other significant elements in these chars using XAFS spectroscopy.

Samples of char and ash from both Radian and UNDEERC were run at the Hg L$_{III}$ edge at 12,284 eV at SSRL during November 1996. Some preliminary data are presented here for mercury in four activated carbon samples from UNDEERC as these samples had by far the highest levels of mercury in them. Furthermore, as we could not detect a useful edge in any other sample, we conclude that the mercury contents were less than 2 ppm in all other samples.

The four samples consist of two composite activated carbons prepared from lignite (LAC-1, LAC-2), a sulfur-impregnated activated carbon (SAC-1), and an iodine-impregnated activated carbon (IAC-1). All four samples had been exposed to the simulated flue gas doped with elemental mercury. Corresponding blank samples (LAC-3, SAC-2, and IAC-2) that had not been exposed to the gas were also supplied.

The mercury XANES spectra for the four carbon samples are shown in Figure 3-21. As with the all mercury XANES spectra, the fine structure is rather subtle and we have resorted to using the first differential of the spectrum to quantify differences among the spectra. As can be seen from the figure, the fine structure becomes more prominent in the order IAC-1 < LAC-1, LAC-2 < SAC-1 and is accompanied by an increasing separation of the two peaks in the first differential spectra. Based on work on other mercury standards, it would appear that the separation of the peaks is highest for ionic mercury compounds and least for covalent and metallic mercury compounds. The observed trend for the peak separation in the activated



| Carbon Form | Step-Height Rel. | Peak Sep'n eV |
|---|---|---|
| SAC-1 | 2.8 | 7.8 |
| LAC-2 | 1.5 | 6.9 |
| LAC-1 | 2.1 | 6.7 |
| IAC-1 | 1.0 | 5.9 |
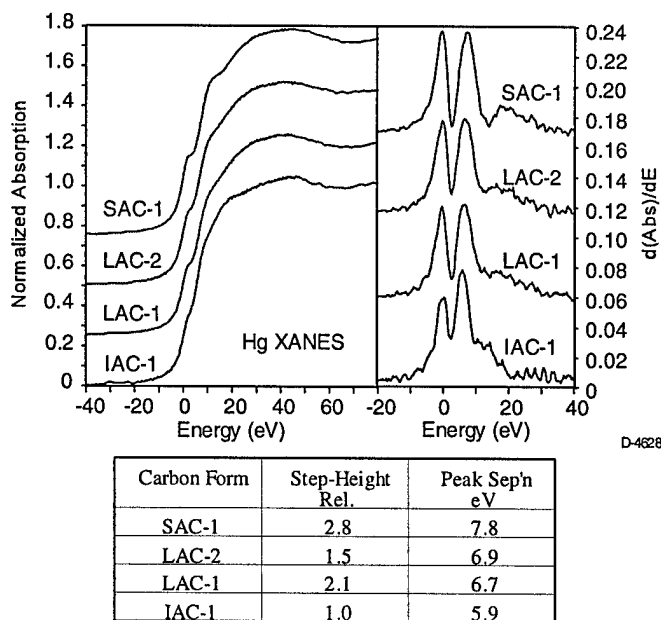
Figure 3-21. Hg XANES spectra and related data for four chars supplied by UNDEERC.

carbons would be consistent with Hg-S bonding in the SAC char and Hg-I bonding in the IAC char. Further evidence for this trend can be seen from an analysis of the EXAFS regions of the XAFS spectra presented in Figure 3-22. The radial structure functions (RSFs) shown in Figure 3-22 indicate a significantly different structure for Hg in the iodine-impregnated carbon. In particular, the Hg-X bond for IAC-1 is much longer than those indicated for Hg in SAC-1 and for LAC-1,2. The bond distance for Hg-I in $HgI_2$ is about 2.78 Å, whereas the Hg-S bond distance in cinnabar (HgS) is about 2.36 Å, the Hg-Cl bond distance in $HgCl_2$ is about 2.25 Å, and the Hg-O bond distance in HgO is about 2.03 Å. Further work is planned to compare the RSFs obtained for the activated carbons with those obtained from mercury standard compounds of known structure.
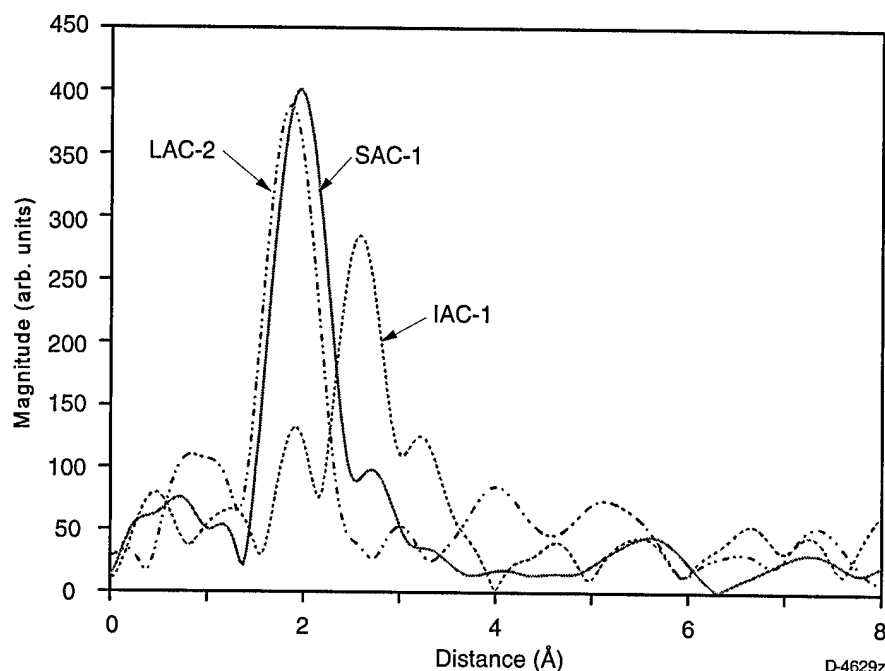


Figure 3-22. Radial structure functions for Hg in three activated carbons.

In addition to data on mercury, XAFS data will also be obtained at the sulfur, calcium, iodine, and possibly other element absorption edges. This will be done in the next XAFS session starting January 27th.

### 3.4.3  Mercury Speciation Measurements

The oxidation state of mercury plays a critical role in its ability to be controlled by air pollution control devices. For example, oxidized mercury is more readily removed in a wet scrubber than elemental mercury. This important fact led to a great deal of work on the measurement of speciation of mercury in flue gas. Equilibrium calculations suggest that mercury is entirely in the elemental form at the high temperatures associated with the combustion zone. As the gas cools equilibrium predicts that the mercury oxidizes. However, as discussed in Quarterly Report No. 4[2] some field data suggests that the mercury oxidation is 'frozen' at some
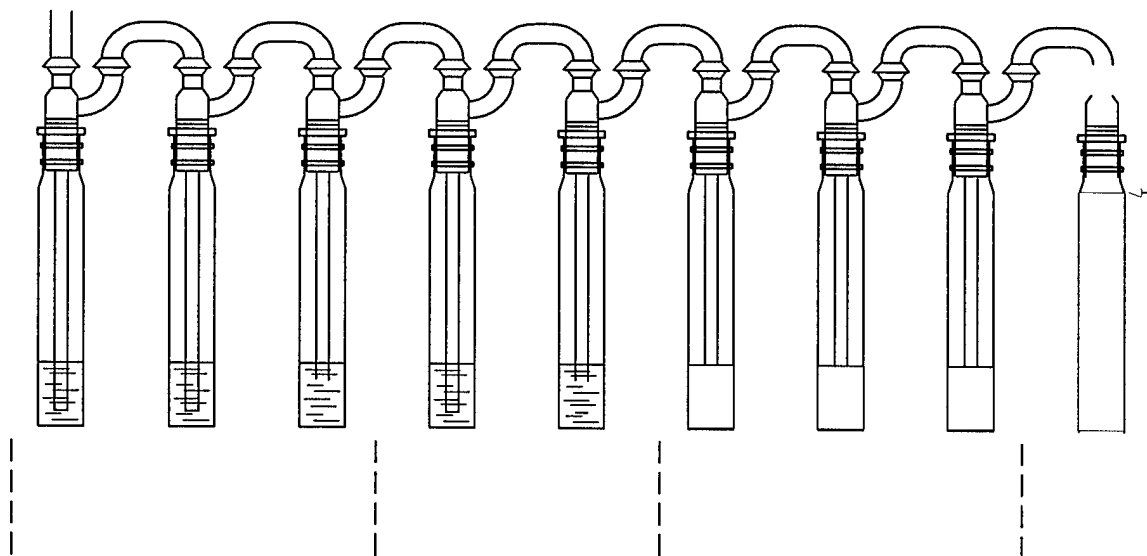
in sam le recover   at the end of the run involved collectin   and wei hin

articulate from the c clone, filter and connectin    lassware.  The   articulate was   laced in

Container #1. Then the   lassware was rinsed with

contents of the KCl im  in

eroxide/nitric acid im  in  ers. The contents of the   otassium   erman anate im  in  ers were

laced in Container #4 then each of these im  in

0.1 nitric acid a                                                  articulate in Container #1 was

then   re  ared b   acid microwave di  estion usin   HF, HCl and HNO  acids then anal  zed for H

the last quarter and described above has helped to further our understanding of trace element

may affect trace element vaporization. XAFS analy

coal indicate that the forms of selenium present differ dramatically between these coals. In the Illinois No. 6 the selenium is predominantly associated with pyrite. In fact, there is a good

ated with pyrite in this coal,

between the various density fractions and the selenium distribution. For the Elkhorn/Hazard coal the primary form of selenium is as organoselenium.

Arsenic leaching data were also used to draw preliminary conclusions about the forms of

Illinois No. 6 and Pittsburgh coals the arsenic was primarily removed with the nitric acid. This result suggests that arsenic is associated with pyrite, a finding which is in agreement with the XAFS data presented in earlier repo                                         ortion of the arsenic was not leached by any of the solvents. One possible explanation for this finding is that the arsenic is associated with finely divided pyrite inclusions which may be shielded from the leaching solution by the carbon. Work is underway to test this explanation.

Combustion testing during the last qu

vaporization is strongly dependent on both the concentration of a given element in coal and the combustion environment. Vaporization data from the MIT drop tube was compared with data from Quann et al. Vaporization was found to increase linearly with trace element concentration

stud of the effect of coal
selection on the amount and com osition of combustion enerated submicron articles,"

# Toxic Substances from Coal Combustion - Forms of Occurrence Analyses

## Technical Progress Report

Reporting Period Start Date: 4/30/96

Reporting Period End Date: 11/1/96

Sharon S. Crowley, Curtis A. Palmer, Allan Kolker, Robert B. Finkelman,
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DE-AI22-95PC95145

U.S. Geological Survey
National Center  MS 956
Reston VA  20192

## Abstract

The overall objective of this project is to provide analytical support for the Physical Sciences, Inc. (PSI) effort being performed under DOE Contract No. DE-AC22-95101 and entitled "Toxic Substances From Coal Combustion - A Comprehensive Assessment". The Pittsburgh, Elkhorn/Hazard, and Illinois No. 6 program coals have been examined to determine the mode of occurrence of selected trace elements using scanning electron microscopy, microprobe analysis, and experimental leaching procedures. Preliminary microprobe data indicates that the arsenic content of pyrite grains in the Illinois No. 6 (0.0-0.027 ppm As) and Pittsburgh (0.0-0.080 ppm As) coals is similar. Pyrite grains observed in the Elkhorn/Hazard coal generally have arsenic concentrations (0.0-0.272 wt. % As) that are slightly higher than those of the Pittsburgh or Illinois No. 6 coals. One pyrite grain observed in the Elkhorn/Hazard coal contained much higher levels of arsenic (approximately 2 wt. % As). Preliminary microprobe analyses and data from leaching experiments indicate the association of arsenic with pyrite in the Pittsburgh and Illinois No. 6 coals. Leaching data for arsenic in the Elkhorn/Hazard coal, in contrast, is inconclusive and additional data are needed before a definite determination can be made.

# Table of Contents

## Introduction

The overall objective of the "Toxic Substances from Coal Combustion - Forms of Occurrence Analyses" project is to provide analytical support for the Physical Sciences, Inc. (PSI) effort being performed under DOE Contract No. DE-AC22-95101 and entitled "Toxic Substances From Coal Combustion - A Comprehensive Assessment". Project goals include (1) developing fundamental mechanistic data, and (2) determining models for the formation, partitioning, and emissions of toxic species from coal combustion. In support of this effort, the United States Geological Survey (USGS) will analyze a number of coal samples utilizing the techni ques described below, to provide information necessary to achieve a better understanding of toxics behavior.

*Phase I*

As a complement to the analyses being performed by PSI under DOE Contract No. DE-AC22-95PC95101, data from a unique protocol developed by the USGS will be used to analyze selected coal size and density fractions for trace element forms of occurrence. In Phase I, the four Phase I coals will be analyzed. The protocol incorporates the elements described below.

All of the samples will be treated by a selective leaching procedure, a powerful technique for approximating modes of occurrence using differing combinations of solvents at various temperatures and concentrations. Splits of the coal will be leached with these solvents (ammonium acetate, hydrochloric acid, hydrofluoric acid, nitric acid) according to the methods developed at the USGS. Results from these leaching tests will provide essential information on chemical bonding of the elements. Elements that are leached by hydrofluoric acid are generally associated with silicates, those that are leached by nitric acid are generally associated with sulfides, and those that are leached by hydrochloric acid are generally associated with carbonates.

Experiments also will be conducted to determine volatility of the elements by heating the coal samples to temperatures ranging from less than 200 ° C to more than 1,000 ° C. A split of each coal sample will be ashed using a low temperature ashing device. This procedure includes oxidation of the coal at temperatures of less than 200 ° C, resulting in a residue of unaltered minerals. This low temperature ash residue will then be chemically analyzed to determine the volatility of the elements at low temperatures. This information, in conjunction with other tests, will provide insight into chemical bonding of the elements present. The low temperature ash will then be used for semi-quantitative mineralogical determination by X-ray diffraction.

The above procedures provide indirect evidence, or approximations of the modes of occurrence of the trace elements in coal. They will be complemented by direct procedures such as manual scanning electron microscopy (SEM) energy dispersive analysis (EDX) of polished pellets of coal. The advantage of the manual method over the automated, computer controlled SEM is that the operator can intelligently select the appropriate phases for analysis by EDX and the operator can apply instantaneous interpretation of the textural relations of the phases being analyzed. The mineralogical, geological, and geochemical expertise of the USGS personnel will provide unique and essential insights.

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For a more sensitive and quantitative analysis, an electron microprobe analyzer will be used. Other, non-routine methods, such as analytical transmission electron microscopy and infrared spectroscopy, will be used as necessary.

**The Agency shall not proceed with any of the work under the Phase II program until formal notification is provided.**

*Phase II*

In Phase II, the Phase II coals will be analyzed. Detailed analysis of coal splits (size and density fractions) from both Phase I and Phase II coals will also be conducted, as required. The standard protocol to be used in Phase II is nearly identical to that used in Phase I; the only significant difference is in the samples to be analyzed. In Phase II, some samples may be subjected to separation procedures and subsequent analysis. For example, density or magnetic separations may be used, or handpicking of specific mineral grains. The protocol to be followed in Phase II incorporates the techniques described below.

Using a methodology similar to that of Phase I, all of the samples will be treated by a selective leaching procedure, using the solvents ammonium acetate, hydrochloric acid, hydrofluoric acid, nitric acid. Results from these leaching tests will provide essential information on chemical bonding of the elements. Experiments to determine volatility of the elements will also be conducted by heating the coal samples to temperatures ranging from less than 200 °C to more than 1,000 °C, using the same procedures as described in Phase I.

These procedures provide indirect evidence, or approximations of the modes of occurrence of the trace elements in coal. As in Phase I, they will be complemented by direct determinations on polished pellets of coal using manual SEM analysis with the EDX analyzer. The mineralogical, geological, and geochemical expertise of the USGS personnel will provide unique and essential insights. For a more sensitive and quantitative analysis, an electron microprobe analyzer will be used. Other, non-routine methods, such as analytical transmission electron microscopy and infrared spectroscopy, will be used as necessary. Also in Phase II, some samples may be subjected to various separation procedures and subsequent analysis. For example, density or magnetic separations may be used or hand picking of specific mineral grains.

**Methods**

(1) Two of the program coals (the Pittsburgh and Elkhorn/Hazard coals) were received by the USGS and shipped to Geochemical Testing of Somerset, Pennsylvania in early May, 1996 for (1) grinding of samples to -20 mesh splits (samples later to be used in petrographic, SEM, and microprobe analysis), (2) grinding of samples to -60 mesh splits (samples to be analyzed by ICP-MS, ICP-AES, hydride generation, and cold vapor atomic absorption), and (3) analysis of sulfur forms. These splits

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were returned by Geochemical Testing and shipped to the USGS, Denver, CO for chemical analysis. The Illinois No. 6 coal was received by the USGS and shipped to Geochemical Testing in early June, 1996, for grinding of samples (as described above) and for analysis of sulfur forms. This sample was returned by Geochemical Testing and shipped for chemical analysis to the USGS, Denver, CO on July 5, 1996. Sulfur form data for each of the three samples is in Appendix I.

(2) Chemical analyses (ICP-AES, ICP-MS) of the three raw coals have been completed.

(3) Representative splits of all program coal samples were ground and cast into pellets and polished for SEM and microprobe analysis according to the procedures outlined by ASTM, (1993) as modified by Pontolillo and Stanton (1994). The casting procedure impregnates, under pressure, approximately 7-8 grams of crushed sample with Armstrong C4 epoxy. The resultant mold is cured overnight at 60° C. A label is incorporated with the sample.

The pellet block is ground and polished using ASTM D2797-85 standards. The epoxy-coal pellet is ground with a 15 $\mu$m diamond platen and 600 SiC grit paper until flat and smooth. Rough polishing is done with 1 $\mu$m alumina and final polishing is completed with 0.06 $\mu$m colloidal silica. Ultrasonic cleaning between and after the various steps insures a final product relatively free of extraneous abrasive material.

Three pellets were prepared from each sample. Each pellet was sectioned with a thin, slow-speed diamond saw and carbon coated for SEM and microprobe analysis.

(4) Each of the three program coals was examined with the SEM with an attached energy dispersive X-ray analyzer (EDXA) to (1) determine major and minor mineralogy of the samples and (2) determine variations in morphology of pyrite grains. Mineral identifications using EDXA are tentative because of its semiquantitative capabilities; however, identification of minerals can be made based on morphology and cleavage characteristics of mineral grains. Because pyrite is known to be a primary source of arsenic in coal (Finkelman, 1994), differing pyrite morphologies were identified in the SEM analysis, for the selection of grains to be analyzed quantitatively with the microprobe. Two types of SEM's were used: an ETEC Autoscan and a JEOL 840[1]. Normal operating voltage was 20 KeV, both secondary electron and back-scattered modes were used.

(5) A fully-automated, 5 spectrometer instrument (JEOL JXA 8800L Superprobe[1]) was used to quantitatively determine element concentrations in sulfides by the wavelength-dispersive technique. In our preliminary microprobe work with the program coals, we measured the following elements: Fe, S, As, Ni, Cu, Zn, and Cd. Natural and synthetic standards were used. Beam current used was 2 x 10 -08 amps; voltage was 20 KeV. The probe diameter was set as a focused beam; the actual working diameter was about 3-5 micrometers. In this study, we considered the minimum detection limit for the microprobe to be at about 100 ppm for each of the elements analyzed, using counting times of 60 seconds for peak and 30 seconds for background for most of the elements. For arsenic, counting times of 90 seconds for peak and 45 seconds for background were used. Trace elements analyzed on the microprobe can be detected at this level; however, counting statistics have a large

uncertainty. In the probe analysis, we attempted to detect compositional differences among different pyrite morphologies. Microprobe data collected are shown in Appendix II.

(6) The sequential selective leaching procedure used in this study is similar to one described by Palmer et al. (1993) which was modified from Finkelman et al. (1990). Duplicate 5g samples were sequentially leached with 35 ml each of 1N ammonium acetate ($CH_3COONH_3$), 3N hydrochloric acid (HCl), concentrated hydrofluoric acid (HF; 48%) and 2N (1:7) nitric acid ($HNO_3$) in 50 ml polypropylene tubes. Each tube was shaken for 18 hrs on a Burrell[b] wrist action shaker. Because of the formation of gas during some of the leaching procedures it was necessary to enclose each tube in two polyethylene bags, each closed with plastic coated wire straps that allow gas to escape but prevent the release of liquid. Approximately 0.5 g of residual solid was removed from each tube for instrumental neutron activation analysis (INAA). The solutions were saved for inductively coupled argon plasma (ICP) analysis.

## Results and Discussion

### SEM and Microprobe Analysis

SEM analysis indicated the presence of the major minerals illite, kaolinite, quartz, and pyrite in each of the program coals (Appendix II). In addition to these four minerals, iron oxides were found in the Pittsburgh coal and calcite was found in the Illinois No. 6 coal. Minor and trace amounts of several other minerals were also observed. Differing morphologies for pyrite were observed in the program coals with the SEM; these morphologies included subhedral grains, euhedral grains, and framboids.

Microprobe analyses indicated that the arsenic content of pyrite grains in the Illinois No. 6 (0.0-0.027 ppm) and Pittsburgh (0.0-0.080 ppm) coals is similar, and that pyrites for these two coals are not distinguishable based on arsenic concentrations. The arsenic concentrations do not appear to vary according to morphology of pyrite grains; however, framboids were not well represented in the microprobe analysis due to their small size (15 micrometers in diameter or less) and difficulty in obtaining a good polish. In general, pyrite grains observed in the Elkhorn/Hazard coal have arsenic concentrations (0.0-0.272 wt. % As) that are slightly higher than those of the Pittsburgh or Illinois No. 6 coals. However, one grain of pyrite observed in the Elkhorn/Hazard coal (analyses 2.1, 2.2, and 2.3, 9/26/96; Appendix III) had a much higher level of arsenic (approximately 2 wt. % As). In future work, elemental mappingusin gthe electron micro probe will be conducted to better characterize the distribution and mode of occurrence of the high arsenic pyrite grains in the Elkhorn/Hazard coal.

Nickel is generally low (0.0 to 0.067 wt. percent) in pyrite of all of the program coals. Two pyrite grains from the Elkhorn/Hazard coal contained higher levels of nickel (approximately 0.1 wt. percent).

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Future microprobe work on the program coals will include broad beam microanalysis of organics to attempt to detect selenium, which is thought to be organically bound (Finkelman, 1994). Other work will involve using SEM image analysis to help determine the distribution of As, Se, or Cr. All data will be used in mass balance calculations of trace element residence.

*Leaching Experiments*

Leaching experiments were completed for the three program coals and the resulting samples (leachate solutions and solid residues) were submitted for chemical analysis. ICP-AES and ICP-MS data (for leachate solutions) and INAA data (for solid residues) have been obtained. The chemical data for leachates have been processed to derive the mean percentages of each element leached by the four leaching agents (ammonium acetate, hydrochloric acid, hydrofluoric acid, and nitric acid) compared to the original concentration of each element in the raw coal (Table 1). The calculated percentages were then used as an indirect method for determining the mode of occurrence of specific trace elements in the coals. We estimate an error of ±25 percent for these data. The calculated percentages in Table 1 are preliminary and subject to revision as new data become available.

Aluminum and potassium are strongly leached by hydrofluoric acid in each of the three program coals; these data suggest an association of aluminum and potassium with silicates (probably kaolinite and illite). Iron is almost entirely leached by nitric acid in the Pittsburgh and Illinois No. 6 coals, indicating the association of iron with pyrite in these samples. Sulfur form analyses corroborate the presence of pyritic sulfur (0.91-1.57 percent; Appendix I) in these coals. In contrast, iron is leached primarily by hydrochloric acid in the Elkhorn/Hazard coal. The data perhaps indicate that oxidation of pyrite occurred with the formation of leachable iron oxides or sulfates. Additional data are necessary before an evelution can be made. Although the leaching percentages indicate that a very small amount of silicon was leached in each of the three program coals, these calculations are misleading because silicon is lost during the drying process used to prepare the leachate samples for ICP-MS and ICP-AES analysis.

Because arsenic in the Pittsburgh and Illinois No. 6 coals was leached primarily by nitric acid, we infer the association of arsenic with pyrite. The association of arsenic with pyrite in these coals is confirmed by microprobe analyses. In the Elkhorn/Hazard coal, arsenic behaves in a manner similar to that of iron; arsenic is leached primarily by hydrochloric acid. It is possible that pyrite grains with high concentrations of arsenic (approximately 2 wt. percent) in the Elkhorn/Hazard were more readily oxidized than grains with low concentrations of arsenic (100 ppm arsenic). However, the arsenic data are incomplete, as indicated by low total percentages for arsenic in the four leachates (about 40 percent) and additional data are needed before a definite determination can be made. Future work may involve the examination of solid residue from the nitric acid leach to determine if some of the arsenic was not leached.

## Conclusion

Phase I of the project is progressing satisfactorily. The USGS has analyzed the three program coals (Pittsburgh, Elkhorn/Hazard, and Illinois No. 6) by using (1) trace element analysis (ICP-AES, ICP-MS, Cold Vapor Atomic Absorption, Hydride Generation), (2) leaching experiments, (3) preliminary SEM analysis, and (4) preliminary microprobe analysis.

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Pontolillo, J. and Stanton, R.W., 1994, Coal petrographic laboratory procedures and safety manual II. *U. S. Geological Survey Open-File Report 94-631*, 69 p.

**Table 1.** Mean percentages of each element leached by various leaching agents (ammonium acetate, hydrochloric acid, hydrofluoric acid, and nitric acid) compared to the original concentration of the element in the raw coal (Pittsburgh, Elkhorn/Hazard, and Illinois No. 6). We estimate an error of ±25 percent for these data. All data are preliminary and subject to revision as new data become available. Am. Ac.=ammonium acetate. Raw coal analyses are in ppm (whole coal basis).

|  | Al | Ca | Fe | K | Mg | Mn | Na | Si | Ti |
|---|---|---|---|---|---|---|---|---|---|
| **Pittsburgh** | | | | | | | | | |
| Raw Coal (ppm) | 8113 | 2347 | 9190 | 787 | 382 | 13 | 542 | 14332 | 407 |
| Am. Ac. | 0 | 75 | 0 | 1 | 40 | 40 | 54 | 0.7 | 0 |
| HCl | 2 | 18 | 4 | 2 | 7 | 18 | 18 | 0.4 | 0 |
| HF | 92 | 4 | 6 | 131 | 41 | 12 | 47 | 0 | 36 |
| HNO$_3$ | 1 | 3 | 106 | 0 | 0 | 42 | 8 | 0.1 | 0 |
| **Elkhorn/Hazard** | | | | | | | | | |
| Raw Coal (ppm) | 12702 | 1257 | 3245 | 929 | 323 | 14 | 320 | 18323 | 719 |
| Am. Ac. | 0 | 49 | 1 | 3 | 21 | 31 | 54 | 1 | 0 |
| HCl | 2 | 19 | 44 | 6 | 16 | 62 | 14 | 0 | 0 |
| HF | 54 | 6 | 15 | 101 | 45 | 11 | 71 | 0 | 18 |
| HNO$_3$ | 0 | 1 | 3 | 0 | 0 | 0 | 25 | 2 | 0 |
| **Illinois No. 6** | | | | | | | | | |
| Raw Coal (ppm) | 9812 | 2797 | 12967 | 1539 | 540 | 37 | 436 | 22629 | 562 |
| Am. Ac. | 0 | 84 | 0 | 3 | 13 | 41 | 42 | 0 | 0 |
| HCl | 1 | 5 | 7 | 3 | 6 | 10 | 13 | 0 | 0 |
| HF | 58 | 2 | 4 | 74 | 20 | 4 | 37 | 0 | 31 |
| HNO$_3$ | 1 | 3 | 98 | 1 | 8 | 19 | 17 | 0 | 0 |

**Table 1.** (Continued) Mean percentages of each element leached by various leaching agents (ammonium acetate, hydrochloric acid, hydrofluoric acid, and nitric acid) compared to the original concentration of the element in the raw coal (Pittsburgh, Elkhorn/Hazard, and Illinois No. 6). We estimate an error of ±25 percent for these data. All data are preliminary and subject to revision as new data become available. Am. Ac.=ammonium acetate. Raw coal analyses are in ppm (whole coal basis).

| | As | Cd | Co | Cr | Cu | Ni | Pb | Sb |
|---|---|---|---|---|---|---|---|---|
| **Pittsburgh** | | | | | | | | |
| Raw Coal (ppm) | 4.7 | 0.06 | 2.4 | 8.8 | 5.3 | 6.6 | 3.1 | 0.29 |
| Am. Ac. 1 | 11 | 0 | 0 | 9 | 10 | 23 | 5 | |
| HCl | 11 | 29 | 15 | 35 | 27 | 200 | 39 | 11 |
| HF | 5 | 20 | 0 | 43 | 7 | 25 | 12 | 19 |
| HNO$_3$ | 57 | 44 | 35 | 55 | 75 | 165 | 60 | 28 |
| **Elkhorn/Hazard** | | | | | | | | |
| Raw Coal (ppm) | 5.1 | 0.06 | 7.0 | 14.4 | 19.2 | 12 | 8.8 | 1.2 |
| Am. Ac. | 1 | 25 | 0 | 0 | 3 | 10 | 10 | 1 |
| HCl | 29 | 56 | 9 | 15 | 25 | 25 | 41 | 3 |
| HF | 6 | 36 | 0 | 24 | 0 | 12 | 6 | 15 |
| HNO$_3$ | 4 | 8 | 0 | 5 | 4 | 16 | 11 | 6 |
| **Illinois No. 6** | | | | | | | | |
| Raw Coal (ppm) | 3.1 | 0.41 | 3.6 | 18.5 | 8.2 | 12.4 | 13.4 | 0.4 |
| Am. Ac. | 1 | 1 | 7 | 0 | 3 | 9 | 15 | 2 |
| HCl | 19 | 25 | 37 | 9 | 11 | 26 | 32 | 5 |
| HF | 5 | 4 | 0 | 20 | 8 | 12 | 7 | 9 |
| HNO$_3$ | 40 | 39 | 29 | 16 | 77 | 104 | 30 | 27 |

Table 1. (Continued) Mean percentages of each element leached by various leaching agents (ammonium acetate, hydrochloric acid, hydrofluoric acid, and nitric acid) compared to the original concentration of the element in the raw coal (Pittsburgh, Elkhorn/Hazard, and Illinois No. 6). We estimate an error of ±25 percent for these data. All data are preliminary and subject to revision as new data become available. Am. Ac.=ammonium acetate. Raw coal analyses are in ppm (whole coal basis).

| | As | Cd | Co | Cr | Cu | Ni | Pb | Sb |
|---|---|---|---|---|---|---|---|---|
| **Pittsburgh** | | | | | | | | |
| Raw Coal (ppm) | 4.7 | 0.06 | 2.4 | 8.8 | 5.3 | 6.6 | 3.1 | 0.29 |
| Am. Ac. 1 | 11 | 0 | 0 | 9 | 10 | 23 | 5 | |
| HCl | 11 | 29 | 15 | 35 | 27 | 200 | 39 | 11 |
| HF | 5 | 20 | 0 | 43 | 7 | 25 | 12 | 19 |
| HNO$_3$ | 57 | 44 | 35 | 55 | 75 | 165 | 60 | 28 |
| **Elkhorn/Hazard** | | | | | | | | |
| Raw Coal (ppm) | 5.1 | 0.06 | 7.0 | 14.4 | 19.2 | 12 | 8.8 | 1.2 |
| Am. Ac. | 1 | 25 | 0 | 0 | 3 | 10 | 10 | 1 |
| HCl | 29 | 56 | 9 | 15 | 25 | 25 | 41 | 3 |
| HF | 6 | 36 | 0 | 24 | 0 | 12 | 6 | 15 |
| HNO$_3$ | 4 | 8 | 0 | 5 | 4 | 16 | 11 | 6 |
| **Illinois No. 6** | | | | | | | | |
| Raw Coal (ppm) | 3.1 | 0.41 | 3.6 | 18.5 | 8.2 | 12.4 | 13.4 | 0.4 |
| Am. Ac. | 1 | 1 | 7 | 0 | 3 | 9 | 15 | 2 |
| HCl | 19 | 25 | 37 | 9 | 11 | 26 | 32 | 5 |
| HF | 5 | 4 | 0 | 20 | 8 | 12 | 7 | 9 |
| HNO$_3$ | 40 | 39 | 29 | 16 | 77 | 104 | 30 | 27 |

**Appendix I.** Sulfur Form Data (all data in percent on a dry basis).

| | Sulfate Sulfur | Pyritic Sulfur | Organic Sulfur | Total S |
|---|---|---|---|---|
| Pittsburgh | 0.01 | 0.91 | 1.20 | 2.12 |
| Elkhorn/Hazard | 0.03 | 0.12 | 0.72 | 0.87 |
| Illinois No. 6 | 0.04 | 1.57 | 2.21 | 3.82 |

**Appendix II. Mineralogy of the three program coals based on SEM analysis.**

### Pittsburgh

| | |
|---|---|
| Major: | Illite, kaolinite, quartz, pyrite, iron oxide |
| Minor/trace: | Barite, $TiO_2$, calcium sulfate (probably gypsum) |

### Elkhorn/Hazard

| | |
|---|---|
| Major: | Illite, kaolinite, quartz, pyrite |
| Minor/trace: | Iron oxide, chalcopyrite, $TiO_2$, barite, apatite, monazite (REE phosphate), zircon. |

### Illinois No. 6

| | |
|---|---|
| Major: | Illite, kaolinite, quartz, pyrite, calcite |
| Minor/trace: | none observed |

**Appendix III.** Quantitative microprobe analyses of pyrite grains in the Pittsburgh, Elkhorn/Hazard, and Illinois No. 6 coals. Subh.=subhedral, euh.=euhedral, irr.= irregular, fram.=framboid, n.d.=no data, no.=analysis number.

**Pittsburgh Coal**

| No. | Date (1996) | Pellet | Morph. of pyrite | Size (μm) | Total (wt.%) | As (wt.%) | Cu (wt.%) | Ni (wt.%) | Zn (wt.%) |
|---|---|---|---|---|---|---|---|---|---|
| 2.3 | 11-26 | altB | subh. | 60x80 | 96.056 | 0.08 | 0 | 0 | 0.012 |
| 3.1 | 11-26 | altB | euh. | 60x60 | 98.11 | 0.005 | 0 | 0 | 0.004 |
| 3.2 | 11-26 | altB | euh. | 60x60 | 98.6 | 0.002 | 0 | 0.003 | 0.013 |
| 3.3 | 11-26 | altB | euh. | 60x60 | 98.36 | 0.0 | 0.01 | 0.016 | 0 |
| 4.1 | 11-26 | altB | subh. | 40x60 | 96.85 | 0.0 | 0 | 0 | 0 |
| 4.2 | 11-26 | altB | subh. | 40x60 | 97.84 | 0.004 | 0 | 0 | 0 |
| 5.1 | 11-26 | altB | subh/irr. | 25x60 | 97.24 | 0.011 | 0.013 | 0 | 0 |
| 5.2 | 11-26 | altB | subh/irr. | 25x60 | 97.69 | 0 | 0 | 0 | 0 |
| 6.1 | 11-26 | altB | subh/irr. | 60x100 | 99.37 | 0 | 0 | 0.009 | 0 |
| 6.2 | 11-26 | altB | subh/irr. | 60x100 | 97.37 | 0.004 | 0 | 0 | 0 |
| 6.3 | 11-26 | altB | subh/irr. | 60x100 | 98.97 | 0.009 | 0 | 0 | 0 |
| 7.1 | 11-26 | altB | euh. | 120 | 98.46 | 0.003 | 0.028 | 0.001 | 0 |
| 7.2 | 11-26 | altB | euh. | 120 | 100.43 | 0.012 | 0.001 | 0.055 | 0 |
| 8.1 | 11-26 | altB | cleat? | 20x60 | 96.75 | 0.0 | 0 | 0.016 | 0 |
| 8.2 | 11-26 | altB | cleat? | 20x60 | 97.86 | 0.0 | 0 | 0.002 | 0 |
| 9.1 | 11-26 | altB | cleat? | 15x70 | 98.17 | 0.016 | 0.016 | 0.013 | 0.003 |
| 9.2 | 11-26 | altB | cleat? | 15x70 | 99.55 | 0.023 | 0 | 0 | 0.011 |
| 10.1 | 11-26 | altB | cleat? | 100 | 99.28 | 0.005 | 0.003 | 0 | 0 |
| 10.2 | 11-26 | altB | euh. | 100 | 98.7 | 0.0 | 0.023 | 0.016 | 0 |
| 10.3 | 11-26 | altB | euh. | 100 | 97.82 | 0.001 | 0.032 | 0.006 | 0.014 |
| 13.1 | 11-26 | altB | euh. | 20 | 98.39 | 0.026 | 0.189 | 0.001 | 0.017 |

**Elkhorn/Hazard**

| No. | Date (1996) | Pellet | Morph. of pyrite | Size (μm) | Total (wt.%) | As (wt.%) | Cu (wt.%) | Ni (wt.%) | Zn (wt.%) |
|-----|------|--------|------------------|------|--------|-------|-------|-------|-------|
| 1.1 | 11-26 | altB | irr. | 40x60 | 95.41 | 0.128 | 0.013 | 0 | 0 |
| 2.1 | 11-26 | altB | irr. | 10x20 | 95.84 | 0.019 | 0.017 | 0.007 | 0 |
| 3.1 | 11-26 | altB | framb. | 10 | 95.92 | 0.124 | 0.024 | 0.038 | 0.002 |
| 4.1 | 11-26 | altB | irr. | 30 | 97.4 | 0.017 | 0.034 | 0.041 | 0 |
| 4.2 | 11-26 | altB | irr. | 30 | 98.33 | 0.021 | 0.038 | 0.15 | 0 |
| 5.1 | 11-26 | altB | framb. | 20 | 97.03 | 0.013 | 0.012 | 0.021 | 0 |
| 5.2 | 11-26 | altB | framb. | 20 | 95.72 | 0.04 | 0.013 | 0.025 | 0 |
| 6.2 | 11-26 | altB | framb. | 30 | 96.03 | 0.053 | 0.006 | 0.102 | 0 |
| 7.1 | 11-26 | altB | subh. | 15 | 96.06 | 0.011 | 0.063 | 0 | 0 |
| 8.1 | 11-26 | altB | cleat? | 5x30 | 98.13 | 0.272 | 0 | 0 | 0 |
| 9.1 | 11-26 | altB | subh. | 70x80 | 98.06 | 0.009 | 0.028 | 0 | 0 |
| 9.2 | 11-26 | altB | subh. | 70x80 | 96.75 | 0.00 | 0 | 0 | 0 |
| 10.1 | 11-26 | altB | subh. | 80x100 | 98.88 | 0.013 | 0.011 | 0 | 0 |
| 10.2 | 11-26 | altB | subh. | 80x100 | 100.2 | 0.0 | 0.001 | 0 | 0 |
| 10.3 | 11-26 | altB | subh. | 80x100 | 99.12 | 0.011 | 0 | 0 | 0 |
| 11.1 | 11-26 | altB | subh. | 30x40 | 96.52 | 0.0 | 0 | 0.016 | 0 |
| 12.1 | 11-26 | altB | sub/euh. | 20x35 | 96.79 | 0.024 | 0.022 | 0.003 | 0.011 |
| 12.2 | 11-26 | altB | sub/euh. | 20x35 | 96.57 | 0.012 | 0 | 0.001 | 0 |
| 2.1 | 9-26 | B | sub/euh. | 30x50 | 98.85 | 1.799 | 0.002 | 0.002 | n.d. |
| 2.2 | 9-26 | B | sub/euh. | 30x50 | 98.71 | 1.971 | 0.006 | 0 | n.d. |
| 2.3 | 9-26 | B | sub/euh. | 30x50 | 98.66 | 2.1 | 0 | 0 | n.d. |

**Illinois No. 6**

| No. | Date (1996) | Pellet | Morph. of pyrite | Size ($\mu$m) | Total (wt.%) | As (wt.%) | Cu (wt.%) | Ni (wt.%) | Zn (wt.%) |
|------|-------|------|--------|-------|--------|-------|-------|-------|-------|
| 1.1 | 11-26 | altB | subh. | 50x60 | 97.48 | 0.002 | 0.026 | 0.048 | 0 |
| 1.2 | 11-26 | altB | subh. | 50x60 | 98.03 | 0.027 | 0.002 | 0.042 | 0.022 |
| 1.3 | 11-26 | altB | subh. | 50x60 | 98.24 | 0.012 | 0.016 | 0.04 | 0 |
| 2.1 | 11-26 | altB | framb. | 25 | 98.01 | 0.008 | 0.008 | 0 | 0 |
| 3.1 | 11-26 | altB | framb. | 20 | 96.11 | 0 | 0.028 | 0.013 | 0 |
| 4.1 | 11-26 | altB | cleat? | 20x70 | 100.13 | 0 | 0 | 0 | 0 |
| 4.2 | 11-26 | altB | cleat? | 20x70 | 100.31 | 0 | 0 | 0 | 0 |
| 7.1 | 11-26 | altB | framb. | 20 | 99.59 | 0.011 | 0.002 | 0 | 0 |
| 11.1 | 11-26 | altB | subh. | 20 | 100.34 | 0 | 0 | 0.008 | 0 |
| 12.1 | 11-26 | altB | framb. | 30 | 98.23 | 0.014 | 0.011 | 0.003 | 0 |
| 12.2 | 11-26 | altB | framb. | 30 | 98.59 | 0 | 0 | 0.012 | 0 |
| 13.1 | 11-26 | altB | euh. | 10 | 95.7 | 0 | 0.077 | 0.067 | 0.003 |
| 14.1 | 11-26 | altB | framb. | 20 | 97.22 | 0.002 | 0.012 | 0.063 | 0 |